ABSTRACT

KATYA BILYK. Enhanced Coagulation Using a New Magnetic Ion Exchange Resin. (Under the direction of Dr. Philip Singer)

The objective of this investigation was to examine the effectiveness of a magnetic ion exchange resin (MIEX®) to enhance the coagulation of disinfection by-product (DBP) precursors in nine surface waters each representing a different element of the EPA's 3x3 enhanced coagulation matrix. The effect of MIEX-treatment on subsequent coagulation with alum was also compared with the coagulation of raw water with alum to determine if there was a reduction in the requisite alum dose for turbidity removal. Ultraviolet absorbance and total organic carbon (TOC) concentration were used as surrogates for the removal of DBP precursors.

Enhanced coagulation with MIEX was found to be very effective for removing trihalomethane (THM) precursors from the nine waters examined. THM formation potential was reduced by more than 60% in all waters studied and reductions in excess of 90% were seen in the waters with the three highest specific ultraviolet absorbance values. The residual TOC concentration, ultraviolet absorbance, and THM formation potential were all substantially lower as a result of MIEX and alum treatment as compared to alum coagulation alone. In addition, haloacetic acid formation potential was substantially lower as a result of MIEX treatment as compared to alum coagulation. This investigation found that MIEX also substantially lowered the coagulant demand of the treated water. This study demonstrated that MIEX was capable of removing bromide from the surface waters examined and that bromide removal decreased as alkalinity increased. The cost-effectiveness of adding a MIEX treatment train onto an existing surface water treatment plant was considered as well. Cost-effectiveness was found to be a function of the size of the water treatment plant and the magnitude of the reduction in alum dose. The interest rate and number of years in the life cycle used to compute the present value of the operating costs were also shown to be important factors in determining if MIEX would be a cost-effective technology to add to a conventional alum coagulation plant.

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CHAPTER 1
INTRODUCTION

Disinfection by-products form when chlorine is added to drinking water for disinfection. Chloroform was the first disinfection by-product (DBP) to be detected in drinking water (Bellar and McAuliffe, 1971; Rook, 1972). Since then, the research of many scientists and engineers has led to a better understanding of DBP formation and control. Some of the milestones include discovering that: (1) trihalomethanes (THMs) and haloacetic acids (HAAs) are the principle DBPs formed from chlorination of water (e.g. Stevens, et al., 1976; Babcock and Singer, 1979; Christman, et al., 1983); (2) alum coagulation removes a significant amount of disinfection by-product precursors from raw water (e.g. Stevens, et al., 1976; Babcock and Singer, 1979); (3) moving the point of chlorination from raw water to settled water is an effective method for reducing chloroform concentrations (e.g. Babcock and Singer, 1979; Young and Singer, 1979); and (4) bromide affects the speciation of THMs and HAAs (e.g. Stevens, et al., 1976; Pourmoghaddas, et al., 1993; Cowman and Singer, 1995). The development of a standard method for quantifying the concentration of total organic halide (TOX) in water was also helpful in assessing the effects of chlorination on overall disinfection by-product formation (Kuhn and Sontheimer, 1973). Research linking TOX production to chloroform formation (e.g. Reckhow, et al., 1990; Singer and Chang, 1989; Martin, 1995) and linking TOC concentrations to THM formation potential (e.g. Stevens, 1976; Babcock and Singer, 1979; Edzwald, et al., 1985) gave the Environmental Protection Agency sufficient evidence to incorporate enhanced coagulation requirements in Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule. The D/DBP rule mandates specific TOC removals by enhanced coagulation based on the TOC and alkalinity of the raw water (see Table 1.1). These mandatory removals are aimed at reducing the public's exposure to potentially carcinogenic and otherwise harmful chemicals by reducing TOC concentrations prior to the point of disinfection (chlorination).

Table 1.1. Stage I TOC Removal Requirments of the D/DBP Rule

TOC	Alkalinity-mg/L as calcium carbonate		
mg/L	0-60.0	>60.0-120.0	>120.0
<2.0	no action	no action	no action
2.0-4.0	35	25	15
4.0-8.0	45	35	25
>8.0	50	40	30

The subject of this investigation is a new magnetic anion exchange resin (MIEX®) capable of removing dissolved organic carbon (natural organic material) from raw water, thereby reducing THM and HAA formation potential. MIEX combines traditional strong base anion exchange properties like quaternary ammonia functional groups, a polyacrylic, macroporous structure, medium pore size and porosity with several unconventional variations such as making the particle size 2 to 5 times smaller than conventional resins. Decreasing the particle size reduces the reliance on slow, intraparticle diffusion that is associated with active sites inside resin beads. As a result, the rate of exchange between dissolved organic carbon (DOC) and the exchangeable ion (chloride) increases because the available surface area for exchange increases. Adding the resin in a continuously mixed flow through reactor similar to a flocculation tank is another variation on the traditional fixed bed ion exchange process.

A major feature of this resin is that it is recoverable. Each bead of resin contains a magnetic compound, which is integrated into the resin structure. This magnetic property can be utilized to separate the resin from settled sludge.

The objective of this investigation was to examine the effectiveness of the MIEX resin to enhance the coagulation of disinfection by-product (DBP) precursors. The effect of MIEX-treatment on subsequent coagulation with alum was also compared with the coagulation of raw water with alum to determine if there was a reduction in the requisite alum dosage for turbidity removal.

It has been well established (e.g. Edzwald, 1979; Randtke, 1981; Edzwald and Van Benschoten, 1990; Edzwald, 1993; White et al., 1997) that, for most natural waters, the concentration of natural organic material tends to control the coagulant dosage

required for effective turbidity (particle) removal. Hence, application of the MIEX resin prior to coagulation was expected to remove a substantial portion of this natural organic material (DOC), thereby lowering the coagulant demand of the water for subsequent coagulation of particulate material. In so doing, the application of MIEX® was also expected to remove a substantial portion of the DBP formation potential of the water.

CHAPTER 2
LITERATURE REVIEW

2.1. FORMATION OF DISINFECTION BY-PRODUCTS FROM NATURAL ORGANIC MATERIAL

The formation of DBPs from the chlorination of water that contains natural organic material (NOM) is affected by the nature and concentration of NOM, pH, contact time, temperature, chlorine dose and residual, and bromide concentration of the source water (e.g. Stevens, et al., 1976; Singer, 1994).

There are several characteristics of NOM that describe its likelihood of behaving as a precursor in DBP formation reactions. These include specific ultraviolet absorbance (SUVA), concentration of total organic carbon (TOC), the relative concentrations of humic and fulvic acids, and the relative concentrations of hydrophobic and hydrophilic NOM. SUVA is defined as the ratio of ultraviolet absorbance at 254 nm (UV254) to dissolved organic carbon (DOC) concentration (L/mg-m). SUVA is a good indicator of the aromatic carbon content of NOM and its possible reactivity to form THMs and TOX as more THMs per unit of DOC are produced as SUVA increases (e.g. Reckhow, et al., 1990; Krasner, et al., 1996; Croue, et al., 1999). TOC concentration has been proposed as another surrogate for THM formation potential (e.g. Stevens, 1976; Babcock and Singer, 1979; Edzwald, 1985) as THM and HAA formation potentials were shown to be directly proportional to TOC concentrations in synthetic solutions prepared from different hydrophobic extracts (e.g. Kavanaugh, 1978; Babcock and Singer, 1979; Edzwald, et al., 1985; Singer, 1999). In addition to SUVA and TOC, the ratio of humic to fulvic acids is important because humic acids are more reactive with chlorine than fulvic acids, and hence produce more THMs (e.g. Trussell and Umphres, 1978; Babcock and Singer, 1979) and TOX (Reckhow, et al., 1990; Oliver and Thurman, 1993; Martin, 1995). Humic substances have a higher aromatic carbon content than fulvic acids, and thus their DBP formation potential is higher (e.g. Babcock and Singer, 1979; Reckhow, et al., 1990; Oliver and Thurman, 1993; Martin, 1995; Croue, et al., 1999; Singer, 1999). Hydrophobic material, which includes humic material, is easier to coagulate than hydrophilic organic carbon (Collins et al., 1986; Semmens and Staples, 1986; Singer and

Harrington, 1993). Singer and Harrington (1993), demonstrated that hydrophobic material accounted for 30 to 70% of the TOC found in most municipal water supplies. How much of this hydrophobic TOC gets removed prior to chlorination can help determine the extent of DBP formation. Thus, recent studies have suggested that the most hydrophilic fractions of NOM (isolated from humic waters) could be stronger THM and HAA precursors than the corresponding hydrophobic NOM in finished waters because a great deal of the hydrophobic fraction is removed prior to chlorination (Hwang, et al., 1999; Croue, et al., 1999).

The pH at which water is chlorinated is another factor that affects DBP formation. The extent of THM production increases as pH increases (e.g. Stevens, et al., 1976; Rook, 1976; Reckhow and Singer, 1984) as does the rate of THM production (e.g. Stevens, et al., 1976; Rook, 1976) because the reaction is base catalyzed (e.g. Coleman, et al., 1975; Reckhow, et al., 1985; Singer and Reckhow, 1999). However, overall TOX production decreases with increasing pH since many halogenated DBPs hydrolyze above pH 8 (e.g. Reckhow and Singer, 1984; Singer, 1994). Like TOX, HAA formation is known to decrease as pH increases (e.g. Reckhow and Singer, 1984; Singer, 1994).

Longer contact times are known to result in higher THM and HAA concentrations when chlorine is in excess (e.g. Stevens, 1976; Reckhow and Singer, 1984; Summers, et al., 1996). By contrast, longer contact times in distribution systems may protect some consumers from haloacetonitriles and haloketones, two other types of DBPs that decay in distribution systems (e.g. Reckhow, et al., 1985; Krasner, et al., 1989). Consumers would be protected in the sense that living farther from the treatment plant meant longer times for haloacetonitrile and haloketone degradation reactions to occur.

Temperature also increases NOM reactivity. Almost all reaction kinetics are faster at higher temperatures, and DBP formation is no exception (e.g. Singer and Reckhow, 1999). Twice as much chloroform was found to form in a given amount of time at 25°C as compared with 3°C (e.g. Stevens, et al., 1976; Rook 1976). Since TOX concentrations increase as chloroform concentrations increase (e.g. Reckhow, et al., 1990), it is reasonable to assume that TOX concentrations would also increase as temperature increased (e.g. Summers, et al., 1996).

Singer (1994), summarized the effects of higher chlorine doses and residuals as typically producing more HAAs than THMs and producing more trihalogenated HAAs than di- and monohalogenated HAAs. More chlorinated THMs and HAAs are also formed as opposed to brominated and mixed brominated and chlorinated species (Symons, et al., 1993; Symons, et al., 1996; Shukairy and Summers, 1996). It was also shown that increasing chlorine doses and residuals increased THM production (e.g. Symons, et al., 1993).

Many researchers have shown that the concentration of bromide ion in natural waters affects the formation of disinfection by-products. Bromide is oxidized by hypochlorous acid (HOCl) to form hypobromous acid (HOBr). HOBr is a better halogenating species than HOCl, hence more organic material becomes reactive and more TTHM are produced as the concentration of bromide increases for a given chlorine dose (e.g. Trussell and Umphres, 1978; Symons, et al., 1981; Symons, et al., 1993). A correlation was drawn between the ratio of the molar concentration of bromide to the molar concentration of TOC and the molar concentration of THMs to the molar concentration of TOC (Trussell and Umphres, 1978). Furthermore, the presence of bromide in chlorinated humic acid solutions was shown to shift the distribution of THMs and HAAs to more brominated and mixed bromo-chloro species (e.g. Symons, et al., 1993 for THMs; Pourmoghaddas, et al., 1993 for HAAs). Following Pourmoghaddas et al.'s work, Cowman and Singer (1995) investigated the effects of bromide ion on the distribution of haloacetic acid species. They found that the concentrations of mono-, di-, and trichloroacetic acid decreased as bromide concentrations increased from 0 to 25 uM. Trichloroacetic acid predominated over di- and monochloroacetic acid in the absence of bromide. As the bromide concentration increased, the concentrations of tri-, di- and monochloroacetic acid decreased while the concentration of mono-, di- and tribromoacetic acid increased. The formation of bromochloro-, dibromochloro-, and bromodichloroacetic acids increased, peaked, and then decreased as the bromide concentration was increased from 0 to 25 uM. The conclusion was that HAA speciation is dependent on the ratio of bromide ion to chlorine applied.

2.2. TECHNOLOGIES USED FOR DBP PRECURSOR REMOVAL

Coagulation, activated carbon adsorption, membrane filtration, and ion exchange are all technologies that have been identified as tools for the control of disinfection by-products by removing the NOM precursors.

Coagulation refers to all the reactions and mechanisms that cause particles to aggregate in a water undergoing treatment. In general, coagulating and settling water prior to chlorination reduces chlorine demand and DBP concentrations in finished water. The coagulation of NOM with alum was found to be effective for the selective removal of DBP precursors (e.g. Kavanaugh, 1978; Babcock and Singer, 1979; Semmens and Field, 1980; Dempsey, et al., 1984; Reckhow and Singer, 1984; Hubel and Edzwald, 1987; Hundt and O'Melia, 1988). For instance, the coagulation of fulvic acid with alum at pH 6.5 resulted in a 70% reduction in chloroform but only a 22% reduction in TOC (Babcock and Singer, 1979). There are a number of other studies that have shown that coagulation selectively removes DBP precursors by showing that percent removals for UV254 are much larger than the corresponding percent removals for TOC (Semmens and Field, 1980; Reckhow and Singer, 1984; Collins, et al., 1985; Edzwald, et al., 1985; Chadik and Amy, 1987; Reckhow and Singer, 1990; Croue, et al., 1993). UV254 is commonly used and widely accepted as a surrogate for the removal of organic carbon and THM precursors (e.g. Edzwald, et al., 1985; Korshin, et al., 1997; Letterman, et al., 1999). Decreases in THM formation potential have also been shown to exceed percent TOC removal by many researchers (e.g. Young and Singer, 1979; Semmens and Field, 1980; Randtke and Jepsen, 1981). Research has also shown that THM precursor removal can be achieved without sacrificing effective turbidity removal (e.g. Chadik and Amy, 1983). Coagulation is discussed in greater detail in the next section.

Granular activated carbon (GAC) adsorption is another tool for precursor removal. Activated carbon has an average pore volume of 0.6-1.8 cm^3/g, an average internal surface area of 1000 m^2/g, an average diameter of 1 to 2.5 mm. Empty bed contact times for GAC range from 5 to 30 minutes (Fettig, 1999). The small footprint of GAC beds is one reason GAC is a popular technology for NOM removal. Jacangelo et al., (1995), and others have shown that between 1,000 and 10,000 bed volumes can be processed before 50% breakthrough occurs. The removal of DBP precursors was shown

to typically track TOC removal in GAC beds (Hooper, et al., 1996; Lykins, et al., 1998). TOC was also found to be a better indicator of precursor breakthrough than UV254 because TOC breakthrough typically occurred prior to DBP breakthrough. By contrast, the concentration of UV-absorbing material in GAC bed effluent did not increase until after DBP breakthrough occurred (Summers, et al., 1994; Solarik, et al., 1995a,b). Decreasing the pH of the water passing through the bed has been shown to increase NOM adsorption significantly (McCreary and Snoeyink, 1980; Randtke and Jepsen, 1982; Weber et al., 1983). Increasing the contact time and decreasing the size of the carbon grains also improved NOM removal (Fettig, 1999).

Membrane separation is a newer type of technology that has become much more cost-competitive with conventional processes in recent years. Nanofiltration is the type of membrane technology most commonly associated for DBP precursor removal (Taylor and Wiesner, 1999). Nanofiltration involves forcing water through a membrane by creating a 5 bar pressure gradient, (approximately 70-100 psi). This process is capable of removing inorganic ions and organic molecules. Specifically, the molecular weight cutoff for nanofiltration is about 200 Daltons (AWWA and ASCE, 1990). Membrane fouling is a potential problem and can be estimated by passing water through a 0.45-*um* Millipore filter with a 47-mm internal diameter at 30 psig to determine a fouling index. The results of this test, designed to measure the rejection efficiency of particles larger than 0.45-um in diameter, are commonly used to determine a silt density index or modified fouling index. These indices are used to estimate the fouling potential and pretreatment requirements for nanofiltration systems (Taylor and Wiesner, 1999). Some appreciation for the frequency of cleanings can also be gained from these indices. A number of studies have shown that nanofiltration is successful at reducing THM formation potential in surface water. Amy, et al., (1990), demonstrated 49-70% removal of THM formation potential when cartridge microfiltration was used prior to nanofiltration, and Laine, et al., (1993) demonstrated 30-90% removal of THM formation potential with cartridge microfiltration upstream of nanofiltration. The latter study also showed that 90% reductions in THM formation potential could be achieved by using ultrafiltration prior to nanofiltration. In contrast, microfiltration has been shown to

achieve only 20% reductions in THM formation potential with no pretreatment and 40-60% reductions with coagulation prior to microfiltration (Parker, 1991).

Anion exchange resins are known to retain NOM by two mechanisms, namely ion exchange and adsorption. Anions are retained in bands or zones in the resin column depending on the resin's affinity for each of the ions (Clifford, 1999). These zones gradually migrate through the column and eventually the ions will appear in the effluent in order of least preferred to most preferred (Clifford, 1999). The use of anion exchange resins for the removal of DOC is not a well established area of research (Clifford, 1999). However, one study demonstrated that 50% removal of THM formation potential could be achieved by anion exchange (Kim and Symons, 1991). Snoeyink (1979) and Afcharian, et al. (1997) have shown that anion exchange resins can remove DOC more efficiently than activated carbon. Teermann and Jekel (1999) also demonstrated DOC reductions of up to 90% using anion exchange resins in batch experiments, and correlated DOC removal to the removal of UV-absorbing NOM on certain commercial resins. From the discussion above, it is understood that the removal of UV-absorbing material is related to the reduction of THM and HAA formation potential. The use of anion exchange resins for the removal of NOM is discussed further below.

2.3. ALUM COAGULATION FOR THE REMOVAL OF TURBIDITY AND NATURAL ORGANIC MATERIAL

2.3.1. Coagulation Chemistry of Alum

Aluminum sulfate, $Al_2(SO_4)_3 \bullet 14\text{-}16H_20$, or alum, is the most common chemical used to remove turbidity and color from natural waters. Its ability to remove turbidity and NOM from water is highly dependent upon its chemistry. Alum dissolves in water to produce aluminum ions which hydrolyze to produce hydroxo-aluminum species, resulting in the release of protons. The pH of the solution decreases, depending on the alkalinity of the water. The hydrolysis reactions occur very quickly, on the order of milliseconds (Amirtharajah and Mills, 1982). The most common soluble hydrolysis species are $Al(OH)^{+2}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-}$, $Al_2(OH)_2^{+4}$, $Al_3(OH)_4^{+5}$, and $Al_{13}O_4(OH)_{24}^{+7}$ (Harrington, 1997). Formation of the insoluble aluminum hydroxide precipitate ($Al(OH)_{3\,(s)}$) is

another product of hydrolysis, with a rate of formation on the order of 1 to 7 seconds (Amirtharajah and Mills, 1982).

Three mechanisms for the removal of dissolved NOM from natural waters have been identified and are widely accepted (Dempsey, et al., 1984; Randtke, 1988; Harrington, 1997).

1. **Precipitation**. NOM forms complexes with dissolved coagulant species and precipitates if the solubility of the complex is exceeded. Stated another way, precipitation is the conversion of a soluble species to a particulate species.
2. **Coprecipitation**. Dissolved NOM adsorbs to the surface of a metal hydroxide precipitate while the precipitate is being formed.
3. **Colloid destabilization**. NOM associated with particles in water is removed when the coagulant neutralizes the negatively charged particles causing them to aggregate. NOM is associated with the particles because it is adsorbed to the surfaces of inorganic material, such as colloidal clay particles.

The third mechanism for NOM removal is not usually an important consideration since most of the organic carbon in natural waters is in dissolved form.

There are several theories on whether precipitation or coprecipitation is predominantly responsible for the removal of organic carbon at different pH values. One study showed that adsorption of NOM to aluminum hydroxide (coprecipitation) is the most important mechanism for NOM removal at all pH values (Dempsey, 1989). Other studies have demonstrated that complexation and direct precipitation predominate at pH's less than 5, and that coprecipitation predominates at pH's above 6.3 (Dempsey, et al., 1984; Edwards and Amirtharajah, 1985; Jekel, 1986; Hundt and O'Melia, 1988; Van Benschoten and Edzwald, 1990; Edwards and Benjamin, 1992). Both methods are equally feasible pathways for NOM removal at pH values between 5 and 6.3. These relationships are best illustrated by looking at a solubility diagram for aluminum, as shown in Figure 2.1 (Letterman, et al., 1999). Aluminum hydroxide is least soluble at pH values of 5.7 to 6.3 at 25°C.

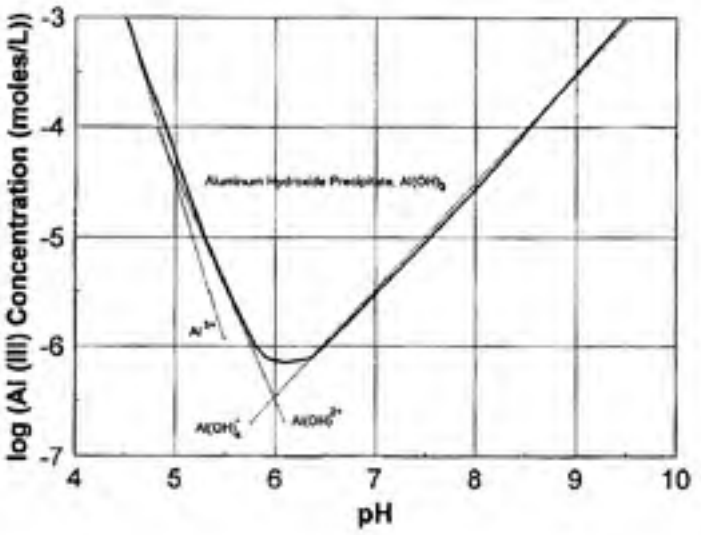

Figure 2.1. The solubility of aluminum as a function of solution pH (25°C).

2.3.2. **Factors Influencing the Coagulation of NOM and Turbidity with Alum**

There are a variety of operational parameters (dosage of coagulant, pH, mixing intensity, etc.) and water quality characteristics (turbidity, TOC, SUVA, temperature, alkalinity, etc.) that can affect the optimization of turbidity and NOM coagulation with alum. Mixing intensity and pH are among the more important operational parameters and TOC and SUVA are arguably the most important water quality characteristics in determining coagulation performance.

Mixing speed in rapid mix basins can dictate whether more soluble or insoluble aluminum hydrolysis species are formed. Plants that want small dense floc, i.e. direct filtration plants, will need to form more of the soluble monomeric and polymeric species. Intense mixing is required because these species form very quickly and it is critical that as much DOC reacts with these species before they hydrolyze further to aluminum hydroxide. Precipitation will be the dominant mechanism for NOM removal for these intense mixing operations. Conversely, plants that want to form large settleable floc will want to form more aluminum hydroxide and thus do not need to provide as great a mixing intensity in rapid mix basins because formation of aluminum hydroxide is not as rapid. Coprecipitation will be the dominant mechanism for NOM removal in basins with lower mixing intensities.

The removal of NOM and turbidity from natural waters using alum as a coagulant is affected by the pH of the solution. Although the aluminum solubility diagram (at 25°C) shows that pH values of 5.7 to 6.3 are optimal conditions for coagulation because Al(III) is least soluble in this range and more hydrolysis species form, research demonstrates that the optimal pH for the removal of TOC and UV-absorbing organic material is around pH 5 (e.g. Babcock and Singer, 1979; Semmens and Field, 1980; Edzwald and Van Benschoten, 1990; Krasner and Amy, 1995). In a study by Krasner and Amy (1995), water from Silver Lake in California showed that optimal coagulation for TOC and turbidity removal occurred at pH 5.25. Lind and Hem (1975) demonstrated that the presence of DOC can significantly change the shape of the aluminum solubility diagram and this may account for the deviation from the theoretically expected optimal coagulation pH. Edzwald and Van Benschoten (1990), showed that for high SUVA waters only half as much alum was required per mg of DOC at pH 5.5 as was required at pH 7. Because of the need to efficiently coagulate TOC and turbidity, it is important to note that the optimum conditions for turbidity and TOC removal are not always the same but good organics removal always coincides with good turbidity removal (e.g. Semmens and Field, 1980). In practice, the optimal pH for coagulation will be specific to each source water and a lot will depend on which mechanism of NOM removal is best suited for the type of organic matter contained in each source water. In general, however, removal of DOC by alum tends to be most effective in the pH range of 5 to 6.

The TOC concentration is an absolute measure of the amount of organic carbon present in the water source. Thus, TOC concentration has been shown to be a good surrogate for the amount of precursor material in a water source (e.g. Stevens, 1976; Babcock and Singer, 1979; Edzwald, 1985). According to White, et al., (1997), there appears to be a linear correlation between the threshold dosage required to initiate turbidity and TOC removal for waters coagulated with alum and the raw water TOC concentration. White, et al., (1997), also showed that water sources with high TOC concentrations and low alkalinities have the least difficulty meeting the performance criteria stated in the EPA's Stage I D/DBP Rule (USEPA, 1998).

SUVA serves as an indicator of the amenability of the organics in a water to removal by coagulation. The coagulant dose required for turbidity and TOC removal in

waters with SUVA values above 4 L/mg-m is controlled by the organic carbon concentration (e.g. Edzwald, 1979; Randtke, 1981; Edzwald and Van Benschoten, 1990; Edzwald, 1993). This behavior has been attributed to organic carbon exerting a coagulant demand that must be satisfied prior to turbidity removal (e.g. Edzwald, 1979; White, et al., 1997). Examining coagulation curves from high SUVA waters shows that TOC concentration and turbidity remain relatively constant until a certain threshold alum dosage is added. Randtke and Jepsen (1981) categorized this behavior as Type I coagulation. Prior to the addition of this critical dosage, UV254 and DOC concentration will decrease suggesting that coagulation is proceeding according to the direct precipitation mechanism (e.g. Edzwald, 1979). In this pathway, soluble aluminum species are complexing with dissolved NOM and precipitation occurs when the solubility of the complex is exceeded. In waters with SUVA values below 3 L/mg-m, the DOC concentration will have a small, if any, effect on the coagulant dose (Edzwald and Van Benschoten, 1990). In these waters, the organic carbon concentration will decrease gradually and tend to plateau as the alum dose increases. This is called Type II coagulation, where no stoichiometric relationship exists between the alum dose required to initiate turbidity and TOC removal and the organic carbon (Randtke and Jepsen, 1981). These waters tend to have a high pH and low concentrations of NOM, which does not exert a coagulant demand prior to turbidity and TOC removal.

2.3.3. The Enhanced Coagulation Rule

Enhanced coagulation is the practice of using a coagulant dose in excess of what is normally required for turbidity removal to achieve a specific reduction in TOC concentration (Bell-Ajy, et al., 2000). The Environmental Protection Agency recently issued Stage I of its Disinfectants and Disinfection By-Products (D/DBP) Rule mandating reductions in TOC concentration based on the TOC and alkalinity of the source water as shown in Table 2.1 (USEPA, 1998). Water facilities treating water by conventional surface water treatment must achieve these percent removals prior to disinfection.

Table 2.1. Stage I TOC Removal Requirements of the D/DBP Rule

TOC mg/L	Alkalinity-mg/L as calcium carbonate		
	0-60.0	>60.0-120.0	>120.0
<2.0	no action	no action	no action
2.0-4.0	35%	25%	15%
>4.0-8.0	45%	35%	25%
>8.0	50%	40%	30%

As was mentioned above, the purpose of the D/DBP Rule is to reduce the public's exposure to potentially harmful compounds that form when NOM reacts with chlorine to form DBPs. Coagulation of NOM with alum or ferric salts is known to be effective for the removal of organic DBP precursors.

Because some utilities treat source waters that are very difficult to coagulate (e.g. low TOC water), the EPA established an alternative performance criterion called the point of diminishing returns (PODR). The PODR is defined as the alum dosage beyond which less than 0.3 mg/L of TOC is removed per 10 mg/L addition of alum (White, et al., 1997). White, et al., (1997) noted that waters that were unable to achieve the requisite percent TOC removals tended to be high alkalinity and/or low TOC waters with low SUVA values. These waters were more likely to need the alternate PODR criterion. They also demonstrated that enhanced coagulation did not interfere with turbidity removal in the waters examined.

2.4. REMOVAL OF NATURAL ORGANIC MATERIAL BY ANION EXCHANGE

Anion exchange resins are produced by attaching positive charges to a crosslinked polymer matrix by covalent bonding. Forty- to sixty-percent of the matrix composition (by weight) is water. These positive charges are usually quaternary amine groups (e.g. $N^+[CH_3]_3$) in the case of strong base anion exchange resins and tertiary amine groups in the case of weak base anion exchange resins. A solution containing a negatively charged ion such as chloride is added in excess to occupy all of the positively charged sites on the

polymer matrix. The negative ions are held in place by electrostatic attraction. For DBP precursor control, the resin is designed so that the selectivity coefficient for NOM over chloride is high and allows the exchange of ions to take place when used in a fixed bed application. Typical operation of ion exchange resins involves passing raw water through a fixed bed of the resin material in either a downflow or upflow orientation. NOM is retained on the resin by either pure ion exchange or adsorption. Adsorption is generally believed to be less important, (e.g. Fu, et al., 1990; Teermann and Jekel, 1999) but some circumstances do favor adsorption. Resins are regenerated when the contaminant ion appears in the effluent at unacceptable concentrations. Regeneration involves flushing the exhausted resin with solutions of very high chloride concentrations that force the ion exchange reaction to run in reverse and thus allows the original resin composition to be restored for another run.

The kinetics of pure ion exchange are based on the theory that the rate of exchange is governed by liquid- and solid-phase resistances to mass transfer. The barrier on the liquid side is modeled conceptually as a stagnant thin film of water surrounding the resin. On the solid side, it is generally believed that the water content of the resin can make resistance to mass transfer rather small as compared to the thin film barrier. Increasing the water content of the resin improves mass transfer and discourages the resin from contracting during regeneration, which reduces its affinity for certain ions. Increasing the water content also makes it easier for NOM to diffuse out of the resin matrix during regeneration (e.g. Semmens, et al., 2000). However, there is a fine line between increasing the water content of the resin and damaging its structural integrity. In essence, there are two ways to improve mass transfer by the pure ion exchange mechanism: (1) shrink the thin boundary layer by providing turbulence in the form of mixing for batch operations; and (2) increase the water content of the resin to reduce resistance to mass transfer on the solid side.

NOM can also be removed by adsorption, although this occurs to a lesser degree in most anion exchange applications. Increasing the ionic strength of the solution can promote the adsorption mechanism due to "salting out" of the NOM onto the resin (e.g. Croue, et al., 1999). Water that was originally part of the resin matrix will diffuse out into the bulk solution and the resin will contract. This will reduce the pore size and pore

size distribution, thereby excluding some of the larger NOM molecules from the matrix. Research has shown that for very large molecules, the size of the anion exchange resin pores and their distribution are the most important factors in determining removal (e.g. Fu and Symons, 1990). The resulting matrix will be more amenable for attracting smaller ions because the pores will be too small for access by the larger NOM molecules.

Various types of resins have been evaluated for their applicability to NOM removal. Special highly porous resins have been used to remove TOC from water (Clifford, 1999). They are effective because high porosity, i.e. more resin-bound water, creates larger spaces for very large NOM molecules on the resin. However, these resins have a drawback because the increased water content weakens the structure of the resin. Fu and Symons (1990) also showed that gel and macroporous resins that are highly crosslinked and very strong were a better structural alternative to the highly porous resins and could be used to remove NOM. In general, strong base anion exchange resins are more useful for removing NOM than weak base anion exchange resins (e.g. Anderson, et al., 1979; Snoeyink, 1979).

2.5. ORICA AND MIEX®

ORICA Australia Pty Ltd is an Australian company that has designed and patented a strong base magnetic ion exchange resin specifically for DOC removal. Orica claims the removal of DOC also lowers the coagulant demand of the water (Morran, et al., 1999).

Orica describes MIEX as having a polyacrylic, macroporous structure that contains quaternary ammonia functional groups. MIEX has a medium pore size and porosity. The particle size is 2-5 times smaller than conventional resins (Slunjski, et al., 2000). Ion exchange is believed to be the dominant mechanism for DOC removal by MIEX.

In full-scale MIEX operations, raw water enters a continuous-flow rapid mix tank ($G \sim 150\ s^{-1}$) with a detention time of about thirty minutes. Resin is continuously fed to the influent water. A settling tank, also called a resin separator, follows the rapid mix tank. Because of the high density of the resin, the overflow rate of this tank is relatively high. Effluent from the resin separator contains product (reduced-TOC) water and a

small amount of carryover resin. Post treatment is still required for turbidity removal because of the carryover resin and because the resin does not remove particles in the raw water; it only removes DOC. Resin is collected from the bottom of the resin separator and passes to a resin regeneration tank where a 10% NaCl solution and a 2% NaOH solution are used to regenerate the resin. According to Orica, 90-percent of the resin is recovered by this procedure. This slurry mode of operation allows the MIEX system to be used on raw water at the front of a conventional surface water treatment plant.

Semmes, et al., (2000), in conjunction with the Saint Paul (Minnesota) Regional Water Services (SPRWS) and Orica Watercare conducted batch and pilot plant studies at the SPRWS. They present several to improve NOM removal kinetics during service and regeneration, some of which were incorporated into their design. These approaches are summarized below.

1. Increase the water content of the resin to reduce contraction during regeneration with concentrated brine.
2. Design the resin in a way that discouraged strong adsorption of the organic ions to the polymer matrix.
3. Reduce the bead size as compared to conventional resins so that NOM does not have to diffuse as far to get in and out of the resin, thereby reducing mass transfer resistance.

The continuous flow pilot plant study at SPRWS demonstrated that MIEX was successful at reducing the TOC concentration and removing UV-absorbing material from raw water (Semmens, et al., 2000). The removals of DOC reduced THM formation potential even when chlorine contact times were five times longer than the current contact time at SPRWS. The study also noted that resin performance dropped 14% during the winter and attributed this to temperature effects and/or altered NOM chemistry.

CHAPTER 3
MATERIALS AND METHODS

3.1. GENERAL APPROACH

In this research, a magnetic ion exchange resin (MIEX) provided by Orica Ltd of Victoria, Australia, was used in enhanced coagulation experiments on nine surface waters to quantify reductions in trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP). Raw water was collected and shipped to the Drinking Water Research Center laboratories at the University of North Carolina in Chapel Hill. Each water came from a utility representing a different element of the 3 x 3 matrix for enhanced coagulation as prescribed in the U.S. Environmental Protection Agency's Disinfectants/Disinfection By-Products (D/DBP) Rule (USEPA, 1998). The utilities that participated in this research are shown in Table 3-1.

Table 3-1. Utilities in Enhanced Coagulation Matrix

Total Organic Carbon (TOC) Concentration mg/L	**Alkalinity, mg/L as $CaCO_3$**		
	0-60	**>60-120**	**>120**
>2-4	Manchester Water Works (Manchester, NH)	Metropolitan Water District (La Verne, CA)	Davis Water Treatment Plant (Austin, TX)
>4-8	Brown Water Treatment Plant (Durham, NC)	Haworth Water Treatment Plant (Hackensack, NJ)	White River Filtration Plant (Indianapolis, IN)
>8	Manatee Water Treatment Plant (Manatee Co., FL)	Tampa Water Department (Tampa, FL)	Sioux Falls Water Purification Plant (Sioux Falls, SD)

The general experimental approach is shown in Figure 3-1. To complete the left treatment train, raw water was initially treated with varying doses of MIEX and samples were collected over a sixty-minute period. These samples were used to determine how UV absorbance decreases as a function of MIEX dose and mixing time. From these results, an optimal MIEX dose and mixing time were determined, where optimal means UV254 absorbance decreased very little with increased mixing time or MIEX dose. Twelve liters of raw water were then batch-treated with the optimal MIEX dose. Finally, alum was used to

coagulate residual turbidity from the batch-treated water. Preliminary coagulation experiments were conducted in 500-mL beakers to determine an optimal alum dose for turbidity removal. A larger volume (2 L) was then treated with the optimal alum dose and set aside for chlorination. To complete the right train, raw water was coagulated in 500-mL beakers with alum to determine an optimal dose. A larger volume (2 L) was then treated with the optimal alum dose and set aside for chlorination.

Chlorination studies were performed on each of the treated saved samples and the raw water, using uniform formation conditions. THM formation and HAA formation were then determined in the chlorinated water.

3.2. GLASSWARE PREPARATION AND REAGENTS

Glassware for general experimental applications was first washed with detergent (Alconox Inc., NY) and warm water. Glassware was then rinsed a minimum of three times with tap water, and placed in a 10% nitric acid bath. Glassware was kept in the acid bath for a minimum of three hours. Afterwards, acid resistant gloves were used to remove the glassware which was then rinsed with deionized organic-free water (DOFW; Dracor Inc., Durham, NC) at least three times. Glassware was then oven-dried for 24 hours at 180°C, while caps were dried at 80°C. The acid-washing and oven-drying steps were omitted on volumetric glassware because the acid and heat would distort their accuracy. Instead, methanol was used to rinse these vessels after the detergent bath and tap water rinse. The methanol rinse took place in a hood and glassware was left overnight in the hood to dry.

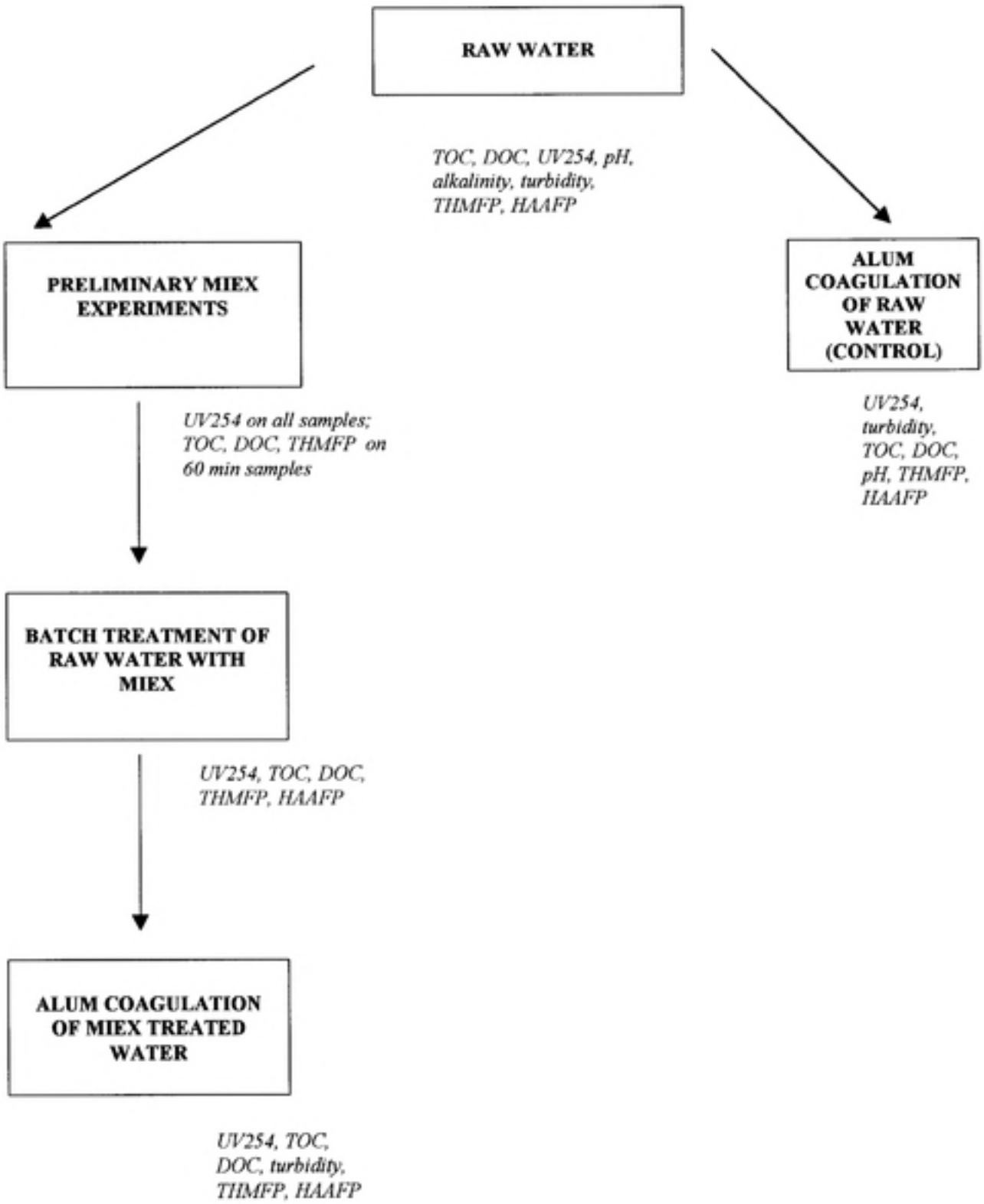

Figure 3.1 General Experimental Approach

The following glassware was prepared chlorine-demand-free: 100-mL volumetric flasks used in pre-chlorination studies, 250-mL Erlenmeyer flasks used to determine the strength of the chlorine stock solution, 300-mL BOD bottles used in final chlorination, and the 40-mL screw cap vials and caps used to quench and store chlorinated water samples. The detergent bath and acid bath steps were employed as stated above. Following drying, glassware was completely submerged in a chlorine bath. This bath was made by adding 80-mL of 4-6 % sodium hypochlorite (Aldrich Chemical Company, Milwaukee, WI) to 10 L of DOFW. Glassware remained in the chlorine bath for at least 3 hours. A minimum of 3 rinses with DOFW followed the chlorine bath. The resulting glassware was chlorine-demand-free, and this was periodically verified by dosing DOFW with 1.0 mg/L of free chlorine, and measuring the free chlorine residual after 24 hours to verify that it was still 1.0 mg/L. This experiment was conducted in 100-mL volumetric flasks approximately once every two or three months. A 1.0 mg/L residual after 24 hours indicated that the glassware and DOFW were both chlorine-demand-free.

All reagents used in this investigation were ACS grade or better.

3.3. RAW WATER

Thirty-gallon plastic drums were used to obtain water from each utility. The drums were cleaned with detergent soap and warm water before shipment. Two drums were shipped by Federal Express from the UNC laboratories in Chapel Hill to one utility at a time. The barrels were filled with water from the influent raw water line, prior to any treatment, and shipped back to the laboratories in Chapel Hill using a common carrier. All waters were refrigerated upon receipt and stored under refrigeration at 4°C until use. All experiments were usually completed within two weeks of receiving the water.

A pump was used to withdraw water from the drums. The pumping rate was approximately 3 L/min. Hard plastic tubing was used for the line from the pump to the drum, and flexible plastic tubing was used for the line from the pump to the collection vessel. A mechanical mixer with swing-out rounded vanes was designed to fit through the narrow 2.5" opening in the drum to mix the water prior to pumping. An initial mix lasted about 20 seconds. Anytime more than 1 L of water was withdrawn from the drum,

pumping stopped while a period of mixing ensued. Mixing and pumping alternated to ensure that the water being withdrawn was representative of the raw water. All water samples were brought to room temperature (23-30°C) prior to experimentation.

Upon receipt, the raw waters were characterized with respect to their turbidity, pH, alkalinity, TOC and DOC concentrations, and ultraviolet absorbance at 254 nm (UV254). A sample of water was also taken for subsequent chlorination and analysis of its THMFP and HAAFP (see below).

3.4. MAGNETIC ION EXCHANGE RESIN

The magnetic ion exchange resin was delivered in slurry form in four 1-L plastic containers. The plastic containers contained approximately 90% resin and 10% carrier water by volume. The four containers were emptied and the contents were combined and stored in a 10-L Nalgene plastic container with 4 L of DOFW. The container had a spigot at the bottom for convenient withdrawal of the resin slurry from the container.

MIEX doses were prepared by first vigorously shaking the Nalgene bottle and filling 10-mL glass graduated cylinders with the slurry. The slurry was given about ten minutes to settle. After this, a specific dose was prepared by adding or removing resin from the graduated cylinder with a glass pipette. For example, to dose 2-L of water with 6 mL/L of MIEX, two 10-mL graduated cylinders were filled with slurry and their settled volumes adjusted to be 6 mL of resin by volume. DOFW was then used to transfer each of the 6-mL volumes of MIEX to the 2-L container. This was necessary because most of the DOFW stored with the resin was lost when MIEX was transferred between 10-mL glass graduated cylinders. Any dry resin on the bottom of the graduated cylinder was immediately resuspended in DOFW and poured into the 2-L jar. Typically 10-mL of DOFW was used to transfer each dose to the raw water. This additional DOFW did not significantly affect the MIEX dose administered.

3.5. MIEX EXPERIMENTS

3.5.1. Preliminary Experiments

Preliminary experiments were conducted for each water to determine the optimal MIEX dose and mixing time. Orica personnel recommended the range of MIEX doses to test based on the TOC concentration of the raw water. For raw waters with TOC concentrations less than 4 mg/L, doses of 2, 4, and 6 mL/L of MIEX were used. For raw waters with TOC concentrations greater than 4 mg/L, MIEX doses of 6, 8, and 10 mL/L were used. When raw water had a TOC concentration of 4 mg/L or higher, MIEX doses of 2 and 4 mL/L were also administered. This allowed for tracking TOC and DOC removal with increasing MIEX dose. A jar containing raw water with no MIEX addition served as a control. This sample is referred to herein as a 0 mL/L dose.

Testing began by filling 2-L square jars with raw water and mixing them at 100 rpm on a Phipps and Bird (Richmond, VA) jar test apparatus. A programmable timer was used to keep track of each jar. The timer for the 0-mL/L control was started first, as soon as mixing began. The lowest MIEX dose was then added to the adjacent jar, and the second timer was started. This was repeated until all jars were appropriately dosed. While the samples were being mixed, aliquots were taken from a sampling port in the side of each jar at mixing times of 5, 10, 20, 30 and 60 min. The samples settled for 30 minutes before being filtered through 0.45 μm filter paper (Supor-450, Gelman Scientific, Ann Arbor, MI) which had been pre-rinsed with 20 mL DOFW. The filtrate was stored in capped 40-mL glass vials. UV254 was measured (see below) for each of the filtered samples. After 60 minutes of mixing and 30 minutes of settling, samples were also taken for TOC and DOC measurement. For the DOC measurements, the samples were first filtered through pre-rinsed 0.45 μm filter paper (Supor-450, Gelman Scientific, Ann Arbor, MI).

After the 60-min mixing period, the remaining water in the 2-L jars was allowed to settle for 30 min after which approximately 1 L of water from the sampling port of each jar was taken and stored for subsequent chlorination and analysis of THMFP. Selected samples were also analyzed for HAAFP. Amber glass bottles were used as

storage vessels and were stored in a refrigerator. Water treated with MIEX was typically chlorinated within two weeks of treatment.

After conducting the preliminary MIEX experiments, UV254 was plotted as a function of mixing time for all the different MIEX doses tested. Based on these results, an optimal MIEX dose and mixing time were selected.

3.5.2. Batch Treatment

Approximately 12 L of raw water were treated with the optimal MIEX dose and mixing time as determined from the preliminary MIEX jar test experiments. The batch treatment was performed in a 20-L glass carboy that was outfitted with a motorized paddle stirrer to transfer a similar amount of energy to the water as was achieved in the jar test apparatus (70 rpm with a 1.5" x 5" rectangular paddle). The carboy also had a sampling port that allowed all but the settled resin to drain out. After mixing, the water was allowed to settle for 30 min and 1 L of settled water was set aside for subsequent chlorination and analysis of THMFP and HAAFP. Three to four liters of the settled water were transferred to 500-mL beakers for subsequent coagulation jar testing experiments with alum. Another 2 L of the settled, batch-treated water was set aside for subsequent coagulation at the optimal alum dosage. Settling removed most of the MIEX beads prior to the coagulation experiments. Samples were also taken for measurement of UV254, TOC, and DOC.

3.6. ALUM COAGULATION PROCEDURES

3.6.1. Coagulation of MIEX-Treated Water

Jar-testing of the MIEX-treated water with alum ($Al_2(SO_4)_3 \cdot (14\text{-}16)H_2O$; Fisher Chemical Co., Fairlawn, NJ) was conducted in 500-mL beakers each fitted with a sample port on the side. A 5 g/L alum dosing solution was prepared by dissolving 0.5 g of alum in 100 mL of DOFW. Following the addition of alum, the waters were subjected to rapid mixing for 1 minute at 100 rpm, flocculation for 20 minutes at 35 rpm, and settling for 30 minutes, after which turbidity was measured.

Turbidity was used to determine the optimal alum dose. Settled water turbidities of between 1.0 and 2.0 were desired. Another 2 L of the MIEX batch-treated water was coagulated in a 2-L square jar at the optimal alum dose using the same coagulation protocol as described above. After settling, one liter of the MIEX- and alum-treated settled water was withdrawn from the sampling port for analysis of turbidity, UV254, TOC, and DOC, and for subsequent chlorination and analysis of THMFP.

3.6.2. Coagulation of Raw Water

As a control, the same coagulation procedure was applied directly to samples of raw water. The pH was maintained above 6 by adding sodium bicarbonate (Fisher Chemical Co., Fairlawn, NJ), if necessary. Different doses of alum were added to a series of 500-mL beakers and the treated waters were rapid-mixed for 1 min at 100 rpm, flocculated for 20 minutes at 35 rpm, and settled for 30 minutes. After selection of the optimal alum dose based on TOC, DOC, turbidity and UV removal, a larger quantity of raw water was coagulated at this alum dose in a 2-L square jar and analyzed for UV254, TOC, and DOC, and for its THMFP and HAAFP following subsequent chlorination. The optimal alum dose was defined as the point where TOC and DOC were no longer appreciably removed with a 5 to 10 mg/L increases in alum dose, provided that settled water turbidities were between 1.0 and 2.0, and UV254 removal was beginning to plateau. If the turbidity was above 2.0 or appreciable UV254 removal was still being achieved a higher alum dose than that required to achieve TOC and DOC removals was chosen.

3.7. CHLORINATION PROCEDURES

3.7.1. Preliminary Chlorination Studies

The chlorine demand of the product water of each process train was determined prior to final chlorination. The method used was based on the uniform formation conditions (UFC) procedure (Summers, et al., 1996). Pre-chlorination studies were typically performed on the raw water, the alum-coagulated water, and the water treated with the lowest MIEX dose that was mixed for 60 min and settled for 30 min.

Preliminary experiments established that the same chlorine dose used for the lowest MIEX dose was also an appropriate choice for the other 60-min MIEX samples, as well as for the MIEX batch-treated water and the MIEX batch-treated water with subsequent alum coagulation. Five chlorine doses were typically examined for each process train. The chlorine doses were based on TOC and UV254 measurements.

A chlorine stock solution was prepared by diluting 5 mL of 4-6% sodium hypochlorite (Aldrich, Chemical Co., St. Louis, MO) in a 100-mL volumetric flask containing DOFW. The strength of the chlorine stock solution was verified using Method 4500-Cl B (Standard Methods 1995). Five milliliters of the chlorine stock solution were diluted in 80 mL of DOFW in a 100-mL chlorine-demand-free volumetric flask. Five milliliters of glacial acetic acid (Fisher Chemical Co., Fairlawn, NJ) were added to the mixture, followed by 1 g of potassium iodide (Fisher Chemical Co., Fairlawn, NJ). The flask was stirred and the solution turned dark yellow. The solution was transferred to a 250-mL chlorine-demand-free Erlenmeyer flask and titrated with 0.1 N sodium thiosulfate (Fisher Chemical Co, Fairlawn, NJ) to a pale yellow endpoint. Then, 1 mL of starch indicator (Fisher Chemical Co., Fairlawn, NJ) was added. The solution turned dark purple in color. The titration with sodium thiosulfate continued until the solution turned clear. Typically between 3 and 5 mL of sodium thiosulfate was required. The strength of the chlorine stock solution was typically between 2000 and 3600 mg/L as chlorine. Simple calculations were then made to determine how much of the stock solution was required to make a 100 mg/L chlorine dosing solution.

The pre-chlorination experiments were conducted in 100-mL, chlorine-demand-free volumetric flasks. The flasks were filled with approximately 80 mL of the water to be tested, and ¼ to 1 mL of pH 8.0 borate buffer was added. The borate buffer was made by dissolving 14.2 g of 1.0 M boric acid in one-liter of DOFW with mixing and heat (Summers, et al., 1996). The pH of the solution was raised to 8.0 with sodium hydroxide. An appropriate volume of chlorine was added from a freshly prepared 100 mg/L sodium hypochlorite dosing solution (see above), after which the flask was filled to the mark with the test water and capped. The chlorinated samples were stored for 24 hours in the dark, in an incubator set at 20°C. After 24 hours, the chlorine residual was measured with a HACH pocket colorimeter (HACH Chemical Co., Loveland, CO). The chlorine dose that

yielded a 1 mg/L residual after 24 hours was the dose chosen for determining the THM and HAA formation potential of the water.

3.7.2. Final Chlorinations

Raw water, alum-coagulated water, raw water treated with different MIEX doses and mixed for 60 min, raw water that was batch-treated with the optimal MIEX dose, and water treated with the optimal MIEX dose and then coagulated with the optimal alum dose were chlorinated in 300-mL glass BOD bottles using the chlorine dose established from the chlorine demand experiments. The samples were buffered at pH 8 with ¼ to 1 mL of borate buffer prior to the addition of chlorine, sealed headspace-free, and incubated at 20°C in the dark for 24 hours. Forty-milliliter screw-cap vials with TFE-lined silicone septa (Laboratory Supply Distributors Corp., Mt. Laurel, NJ) were prepared with about 8-12 granules of ammonium sulfate (Mallinckrodt, Paris, KY) added to quench the chlorine residual. After 24 hours, the free chlorine residual was measured with the HACH pocket colorimeter and the vials were filled with the appropriate sample headspace-free and sealed. These samples were stored in the refrigerator for no longer than 2 weeks. Extractions of chlorinated samples for THM and HAA analysis typically occurred within 3 days. Duplicate vials were stored for each analysis.

3.8. ANALYTICAL METHODS

3.8.1. THM Analysis ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$)

Trihalomethanes were extracted with pentane (THM Grade, Aldrich Chemical Co., St. Louis, MO) and analyzed by gas chromatography using Method 6232B (Standard Methods, 1998). A Hewlett Packard 5890A Series II Gas Chromatograph with an electron capture detector (Hewlett Packard Company, Cary, NC) was employed for the measurement. All procedures were carried out inside a laboratory hood while wearing gloves and safety glasses.

3.8.1.1. Preparation of Calibration Standards

A 2000 ug/L stock solution of THM4 standards (Supelco, Inc., Bellefonte, PA) was used to prepare two dilutions. A 10 mg/L dilution, referred to as dilution 1, was prepared by adding 10 ul of the 2000 ug/L stock to a 2-mL volumetric flask containing high purity THM-free methanol (Burdick & Jackson, Krackler Scientific, Muskegon, MI). A micropipettor with disposable glass tips was used for the transfer. The tip was pre-washed with methanol by pipetting 10 uL of methanol, wiping the sides quickly with tissue paper, wasting the methanol into a beaker designated for methanol waste, and wiping the sides again with tissue paper. A 100 mg/L dilution, referred to as dilution 2, was prepared by adding 100 ul of stock to a 2-mL volumetric flask containing high purity THM-free methanol. The same pre-washing step was used. Following the addition of the standards, both flasks were filled to the line with methanol using a Pasteur pipette. The flasks were then capped and inverted three times to homogenize the concentration in each flask. Dilutions 1 and 2 were then transferred to 4-mL acid-washed amber vials using clean disposable glass pipettes, capped, and stored in a freezer for up to two weeks. After 2 weeks, new dilutions were made. After 3 months, new standards were ordered. Teflon tape was wrapped around the sides and top of the caps to minimize volatilization.

Table 3.2 shows the volume of dilutions 1 and 2 that was transferred to 100-mL volumetric flasks containing approximately 98 mL of DOFW to create the calibration points. Dilutions 1 and 2 were removed from the freezer and allowed to come to room temperature one hour prior to calibration curve preparation.

Table 3.2. Calibration Curve Preparation

Calibration Point (ug/L)	uL of Dilution 1	Calibration Point (ug/L)	uL of Dilution 2
0	0	25	25
1	10	50	50
2	20	100	100
5	50	250	250
10	100		

To create the 1 ug/L calibration point, teflon tape was removed from dilution 1, and the cap was loosened. The micropipettor was set at 10 uL and methanol was used to pre-wash the glass tip. The stopper on the 100-mL flask marked "1 ug/L" was removed. The tip of the micropipettor was inserted into dilution 1, and 10 uL were extracted. The hand not holding the micropipettor was used to replace the cap on dilution 1. The sides of the glass tip were wiped with tissue paper. The tip of the micropipettor was submerged in the DOFW that half-filled the neck of the volumetric flask, and the entire contents of the micropipettor were transferred to the flask. The micropipettor was swirled around a few times with the plunger still fully extended in the DOFW before being removed. With the micropipettor plunger still fully extended, the sides of the tip were wiped. The plunger was then released. The cap to dilution 1 was screwed back on, and the stopper was replaced on the volumetric flask. This entire sequence took place very quickly. This same procedure was repeated for all the calibration points. The final step was to fill the volumetric flasks to the mark with DOFW from a squirt bottle, and invert the flasks three times to homogenize the contents.

3.8.1.2. Preparation of the Pentane and Internal Standard Solution

1,2-dibromopropane (Sigma Chemical, Bellefonte, PA) was used as the internal standard (IS). From the density (ρ=1.937 g/cm^3), calculations were made to determine what dilutions were necessary to create a final solution with a concentration such that adding 100 uL of it to 200 mL of pentane (THM-Grade, Aldrich Chemical Co., St. Louis, MO) would yield a final concentration of 60 ug/L. A 19,370 mg/L dilution, referred to as dilution 1, was prepared by transferring 100 uL of the 5% standard stock solution to a 10-mL volumetric flask containing methanol. A pre-washed glass micropipettor tip was used to prepare the IS dilution. A Pasteur pipette was used to fill the flask to the line with methanol. The flask was then capped and inverted three times to mix. A 120 mg/L dilution, referred to as dilution 2, was prepared by transferring 62-uL of dilution 1 to a 10-mL volumetric flask containing methanol. The glass micropipettor tip was washed with methanol and used in the transfer. A Pasteur pipette was used to fill the flask to the line with methanol. The flask was then capped and inverted three times to mix. The

resulting solution was capped in 4-mL amber vials, wrapped with teflon tape, and stored in the freezer. Dilution 2 was removed from the freezer and allowed to come to room temperature one hour prior to extraction.

The solvent used in these extractions was pentane. A sample from each pentane bottle was analyzed on the gas chromatograph prior to the above steps to ensure that it was THM-free. This involved taking a small aliquot of pentane from a newly opened bottle and sealing it in a 1.8-mL vial. Running the same THM sequence used on water samples and not seeing any peaks at the retention times for chloroform, bromodichloromethane, dibromochloromethane, and bromoform meant the pentane was pure.

To improve speed and accuracy in the extraction process, all of the pentane and IS was transferred to an 800-mL amber jar with an autopipettor mounted on the lid of the jar. From this jar, 4 mL of pentane and IS were transferred efficiently to each sample. First, the volume of pentane required for extractions was calculated. Every sample required 4 mL, and about 40 mL was added to that volume to ensure that no air would become entrained in the autopipettor line as the fluid level reached the bottom of the jar. After the appropriate amount of pentane was added to the jar, the jar was immediately capped, as pentane is highly volatile. Teflon tape was unwrapped from dilution 2 of the IS and the cap was loosened. The micropipettor was set at 100 uL and methanol was used to pre-wash the glass tip. The tip of the pipette was inserted into dilution 2, and 100 uL were extracted. The hand not holding the micropipettor was used to replace the cap on dilution 2. The sides of the glass tip were wiped with tissue paper. The amber jar containing the pentane was unscrewed, the tip of the micropipettor was submerged, and the entire volume of the micropipettor was transferred to the flask. The micropipettor was swirled around a few times with the plunger still fully extended in the pentane before being removed. With the micropipettor plunger still fully extended, the sides of the tip were wiped. The plunger was then released. The lid of the jar was screwed back on tightly and sealed with teflon tape. The cap to dilution 2 was screwed tightly. This entire sequence took place very quickly. The final step was to swirl the contents of the jar for several seconds to mix the IS throughout the pentane.

3.8.1.3. Extraction of Unknowns

The 40-mL vials containing the chlorinated water samples (in duplicate) were removed from the refrigerator at least one hour prior to extraction. Twenty-milliliters of each sample and calibration standard was transferred to another 40-mL acid-washed vial. Twenty-milliliter aliqots were measured with a clean graduated cylinder. Calibration points were extracted in duplicate, i.e. two vials were prepared for each point.

Four milliliters of pentane + IS were added from the autopipettor on the amber jar to each 20-mL sample. The procedure was to unscrew the cap on the 40-mL vial, raise the plunger on the autopipettor, place the vial under the spout, depress the plunger, and cap the vial. Any time an air bubble appeared in the micropipettor line, pentane was wasted to a beaker marked "pentane waste" to clear the line of entrained air. Six grams of anhydrous sodium sulfate (certified ACS Grade, Mallinckrodt, Paris, KY) that was previously baked for 24 hours at 400°C was added to each sample to enhance extraction efficiency. The procedure was to measure out six grams of sodium sulfate, uncap 2 vials, and pour the contents into the vials. Then the samples were quickly capped, shaken and vortexed (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for 60 seconds. This was repeated until all samples contained sodium sulfate and had been vortexed. Separation of the pentane and water layers occurred almost immediately following the vortex step.

The top layer from each sample was transferred to a 1.8-mL glass vial (Fisher Scientific, Pittsburgh, PA) using a Pasteur pipette. The same pipette was used for duplicates, but a clean pipette was used for each separate sample. Vials were filled to the 1-mL mark, and then immediately capped with an aluminum TFE-faced seal (Fisher Scientific, Pittsburgh, PA). After crimping, the cap was turned to see if it would twist. Twisting was indicative of a bad seal, and the crimper was used again until the cap no longer moved on the vial.

The 1.8-mL vials were stored in the freezer until they were analyzed on the gas chromatograph (GC). Samples were analyzed within a few days of extraction

3.8.1.4. GC Operational Parameters

Table 3.3 details the parameters that were used for operation of the GC. .

Table 3.3. GC Operational Parameters

Column	Type: DB-1 fused silica capillary (J&W Scientific, Folsom, CA) Length: 30 m Internal diameter: 0.25 mm Film thickness: 1 um
Temperature program	Hold temperature at 35°C for 10 minutes. Increase temperature from 35°C to 150°@ 10°C/min (11.5 min). Increase temperature from 150°C to 250°C @ 25°C/min (4 min). Hold temperature at 250°C for 1 minute. Total run time is 26.5 min.
Injector	Injection volume : 2 uL Temperature: 180°C
Detector	Type: electron capture Temperature: 280°C
Carrier gas	Helium (99.999+% purity; Holox, Morrisville, NC) Flow rate: 1.0 mL/min @ 35°C
Make-up gas	Nitrogen (99.999+% purity; Holox, Morrisville, NC) Flow rate: 30 mL/min

The GC output was a chromatograph with peak area counts. The peak areas were normalized to the area under the internal standard peak, i.e. relative peak areas were computed. A calibration curve was prepared by plotting the known concentrations of the standards against the peak areas normalized to the internal standard areas for each of the four THM species. The unknowns were quantified by comparing their normalized peak areas with the calibration curve. Replicates that were within 10% of each other were averaged. Replicates that were not within 10% were rechlorinated and extracted again.

3.8.2. HAA Analysis

Haloacetic acids were analyzed using Method 6251B, the micro liquid-liquid extraction gas chromatographic method (Standard Methods, 1998). This procedure was conducted by other laboratory personnel.

All nine haloacetic acids were analyzed using the diazomethane derivatization process. Magnesium sulfate was used as a drying agent (after Brophy, 1999). Standards were obtained as a mixture of HAA6 in methanol, and as separate neat compounds of bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid (Supelco, Inc., Bellafonte, PA). The standards were dissolved in methyl-tert-butyl ether (ultra resi-analyzed grade, J.T. Baker, Phillipsburg, NJ) and a calibration curve was prepared in a similar manner to the THM calibration curve. 1,2,3-trichloropropane (Aldrich Chemical Co., St. Louis, MO) was used as the internal standard, and 2,3-dibromopropionic acid (Supelco, Inc., Bellafonte, PA) was used as a surrogate in the procedure. The surrogate was added to detect problems with derivatization. Good surrogate recovery implies that each calibrator and sample had been successfully derivatized. Unknowns were quantified by comparing normalized peak areas to the calibration curve. A Hewlett Packard 5890A Series II Gas Chromatograph with an electron caputure detector (Hewlett Packard Company, Cary, NC) was employed for the measurement.

3.8.3. Total Organic Carbon and Dissolved Organic Carbon Analysis

TOC and DOC were measured using a Shimadzu 5000 Organic Carbon Analyzer (Shimadzu, Atlanta, GA). Standards in the range of 1-20 mg/L as C of potassium acid phthalate were used for calibration of the instrument. A four-point calibration curve was used for each analytical measurement. At least two injections per calibration standard were made. A third injection was warranted if the coefficient of variation was greater than 2% and the standard deviation of the peak area count was greater than 200. Otherwise, the two injections were considered statistically equivalent and the next sample was analyzed. DOC measurements were made after filtering the samples through pre-rinsed 0.45 μm membrane filters (Supor-450, Gelman Sciences, Ann Arbor, MI). A fresh filter was used for each sample.

The Shimadzu worked by measuring the non-purgeable organic carbon in each sample. Samples were transferred to 5-mL glass test tubes. Two drops of 2 N hydrochloric acid (Fisher Chemical Co., Fairlawn, NJ) were added to each sample to lower the pH to between 2 and 3. Five minutes of sparging with high purity air (Holox Company, Morrisville, NC) followed acid addition. This was done to get rid of any inorganic carbon. The resulting solution was then analyzed by the instrument to determine the organic carbon content in the sample.

A 1000 mg/L TOC stock solution was made by dissolving 2.125 g of reagent-grade anhydrous potassium hydrogen phthalate $C_6H_4(COOK)(COOH)$; (Nacalai Tesque, Inc., Hyoto Japan) in 1000 mL of DOFW. The solution was stored in the refrigerator for up to one year.

3.8.4. Ultraviolet Absorbance

UV absorbance measurements were made using 1 cm quartz cells and a Hitachi 2000 UV-Visible Spectrophotometer (Hitachi Instruments, Danbury, CT). Samples were first filtered through pre-rinsed 0.45 μm membrane filters (Supor-450, Gelman Sciences, Ann Arbor, MI). A fresh filter was used for each sample. A sample of DOFW was used to zero the instrument before any samples were analyzed. The quartz cells were rinsed two times with every new sample before the sample was analyzed. Whenever possible, samples were analyzed from the lowest UV absorbance to the highest UV absorbance to further prevent contaminating the cell. Two measurements were made for each sample and the average is the reported value.

3.8.5. Turbidity Measurements

A HACH 2100P turbidimeter (HACH Chemical Co., Loveland, CO). was used to measure turbidity. HACH GELEX® Turbidity Standards (HACH Chemical Co., Loveland, CO) were used to calibrate the instrument.

3.8.6. Analytical Quality Control

All measurements (TOC, DOC, UV, THMs, HAAs) were made in duplicate. The average of the two measurements is the reported value. Only duplicates that were within 10 percent of each other are reported. In the case of THM extractions, samples were often extracted in triplicate. When two measurements were not within 10 percent of each other, the third sample was analyzed to resolve the disparity. If two out of the three samples were within ten percent of each other, the third value was discarded. If two out of three values were not within 10% of each other, no value was reported.

CHAPTER 4
RESULTS AND DISCUSSION

Table 4.1 summarizes the water quality characteristics for each raw water that was analyzed in this investigation.

Table 4.1. Raw Water Quality Characteristics

Location of Participating Utility	pH	Alkalinity (mg/L as $CaCO_3$)	TOC (mg/L)	DOC (mg/L)	UV254 (1/cm)	Turbidity (NTU)	Br^- (ug/L)
Durham, NC	6.7	20	5.1	5.0	0.175	6.7	18.8
Manatee Co., FL	7.2	20	10.6	10.6	0.477	3.0	163
Indianapolis, IN	8.2	155	4.6	nm	0.088	2.7	38.1
Hackensack, NJ	7.7	95	4.3	3.9	0.106	7.1	42.5
Manchester, NH	6.1	4	2.6	2.1	0.030	1.9	13.7
Sioux Falls, SD	8.1	205	8.7	5.0	0.135	55	91.2
MWD, CA	7.8	73	2.8	2.7	0.081	7.7	215
Austin, TX	7.9	>120	2.8	2.8	0.056	4.1	236
Tampa, FL	7.3	91	26.4	27.3	1.096	3.4	94.5

nm = not measured

4.1. REMOVAL OF NOM WITH MIEX

UV254 has been shown in the literature to be a good surrogate for estimating the amount of organic carbon in raw waters (e.g. Rook, 1982; Edzwald, et al., 1985). Thus, UV254 absorbance was chosen as a surrogate parameter for tracking organic carbon removal with MIEX. Figures 4.1 and 4.2 show the effects of MIEX dose and mixing time on the removal of UV-absorbing organic material for Indianapolis and Sioux Falls water, respectively. Sioux Falls had a higher TOC concentration and UV absorbance than Indianapolis, and therefore higher MIEX doses were chosen for Sioux Falls water. Both figures show that UV absorbance decreased as mixing time and MIEX dose

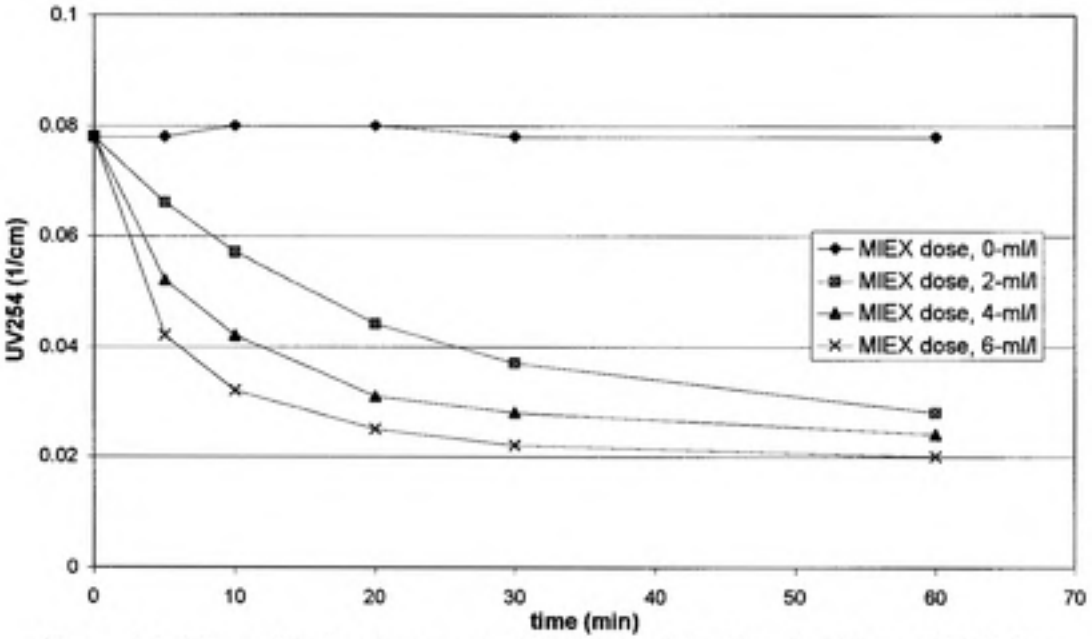

Figure 4.1. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Indianapolis, Indiana.

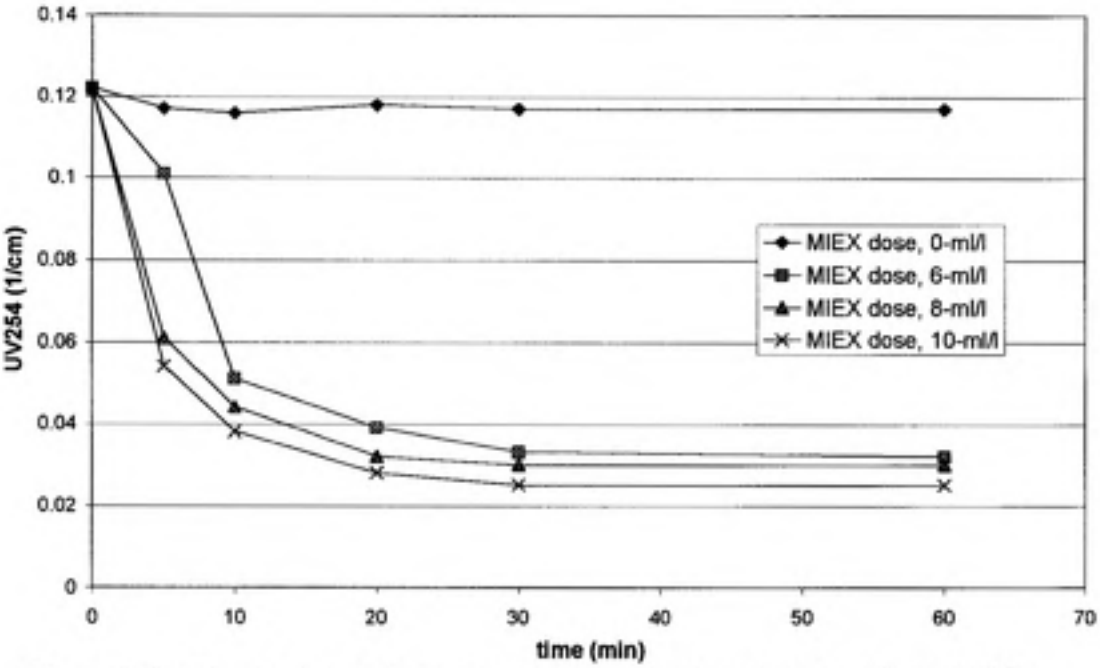

Figure 4.2. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Sioux Falls, South Dakota.

increased. UV absorbance dropped to 0.020 cm^{-1} for Indianapolis (from 0.088 cm^{-1}) and to 0.026 cm^{-1} for Sioux Falls (from 0.135 cm^{-1}). That corresponds to approximately 75% removal of UV-absorbing organic material for Indianapolis and 80% removal for Sioux Falls. Similar removals were achieved in the other seven waters studied (see Appendix A). There was no observable change in pH as a result of MIEX treatment. Figures 4.1 and 4.2 show that the majority of the UV254 removal occurred in the first 20-30 minutes of mixing. Orica also specifies 30 minutes as a typical detention time for full-scale reactors (Slunjski, et al., 2000). According to Orica, thirty minutes of mixing is optimal for ion exchange with easily removable hydrophobic and hydrophilic NOM, but not long enough for significant adsorption to occur. By allowing ion exchange to dominate over adsorption as the mechanism for NOM removal, the resin can be regenerated easily.

Many strong- and weak-base anion exchange resins have been found to be capable of removing disinfection by-product precursors from raw water (Clifford, et al., 1999). Rook and Evans (1979) used a weak base resin to achieve 75% removal of chloroform formation potential and 65% removal of THM formation potential. Likewise, Kim and Symons (1991) found that a combination of ion exchange and granular activated carbon (GAC) adsorption removed about 93% of the influent TOC and 96% of the influent THMFP.

Based on these findings, a reduction in THMFP and HAAFP with MIEX, a strong-base anion exchange resin, was expected. Indeed, Figure 4.3 illustrates: (1) the concentration of THMs formed upon subsequent chlorination decreased as MIEX dose increased; and (2) MIEX reduced THM formation potential after 60 minutes of mixing by 84% for Tampa, 72% for Sioux Falls, 71% for Durham, 78% for Metropolitan Water District, and 78% for Austin (using the highest MIEX doses tested). Similar reductions in THM formation potential were observed in the other waters (see Appendix B). Figure 4.4 shows that MIEX treatment for 20 to 30 minutes reduced HAA formation potential by 46% for Sioux Falls, 79% for Metropolitan Water District, 80% for Austin, and 59% for Manchester. If HAA formation potential had been measured after 60 min of mixing and if the same doses had been used as in Figure 4.3, these percent reductions would likely have been higher. Therefore, MIEX is effective in removing HAA precursors as well as THM precursors.

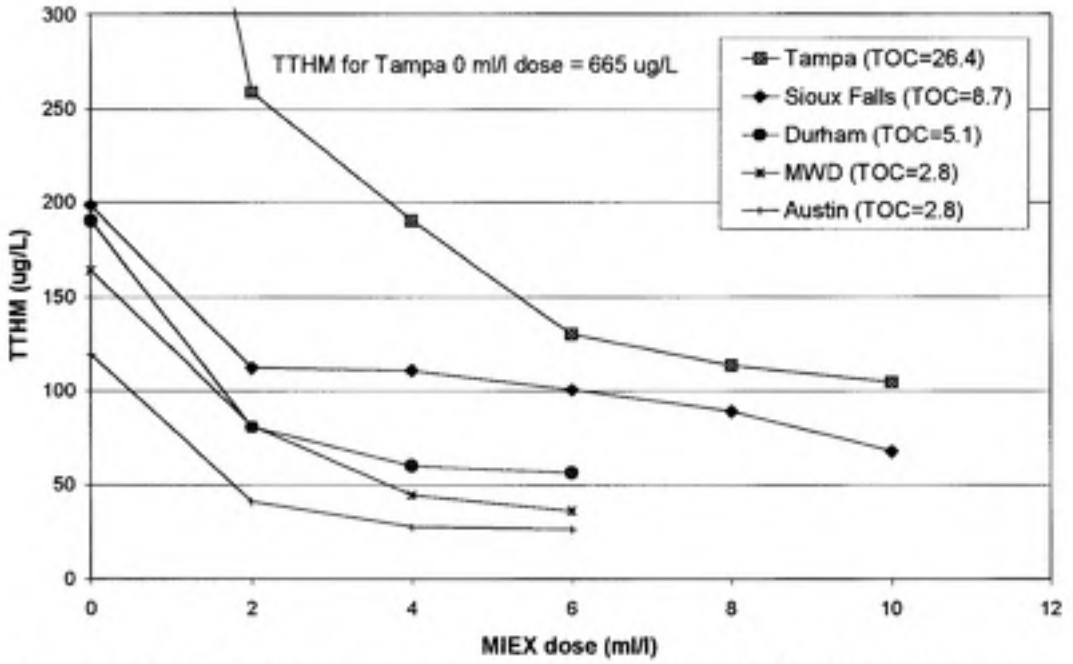

Figure 4.3. TTHM concentration as a function of increasing MIEX dose for several raw waters.

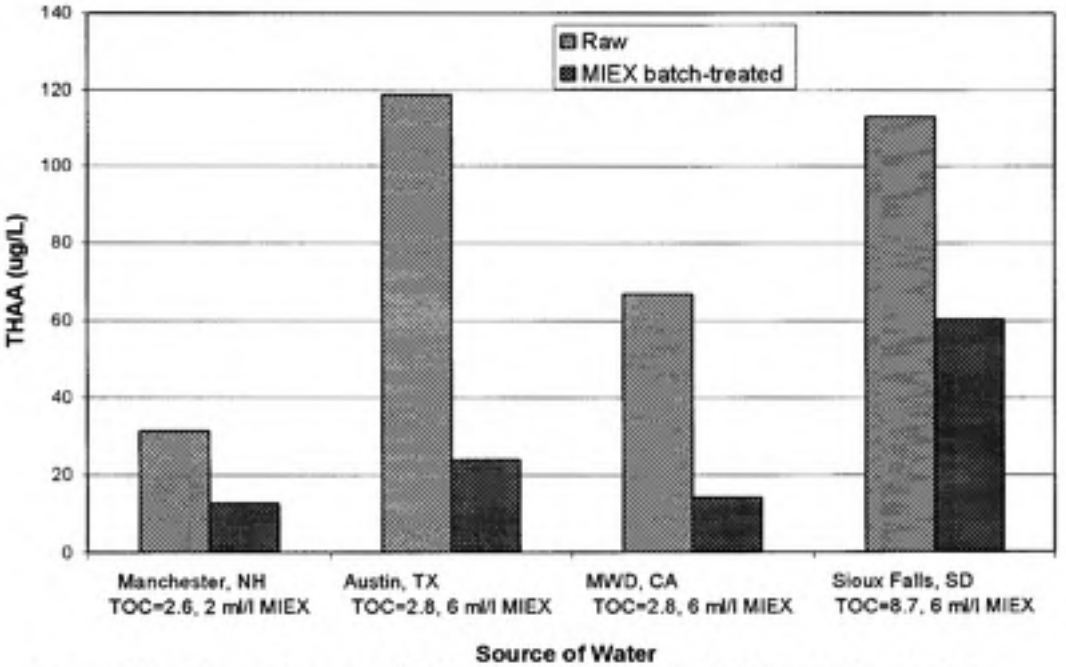

Figure 4.4. Comparison of THAA in raw water and MIEX-treated water for several raw waters.

In addition to being a good surrogate parameter for organic carbon, UV254 has also been shown to reflect THM precursor concentrations in water (e.g. Edzwald, et al., 1985). Figures 4.5 and 4.6 show that the removal of UV-absorbing substances for Sioux Falls and Tampa appears to track the decrease in THM and HAA formation potential, respectively. Similar trends were observed for THM formation potential in the other waters, although not all graphs show as strong a trend as Figures 4.5 and 4.6. HAA data were more limited, but the similarities between Figures 4.5 and 4.6 provide strong evidence that if UV254 removal tracked reductions in THM formation potential and HAA formation potential for Tampa, HAA formation potential probably decreased as MIEX dose increased in the other eight waters. UV254 and TTHM concentrations decrease as MIEX dose increases because more surface area (exchange sites) is (are) being provided for a given amount of mixing time and, accordingly, more organic carbon is removed.

TOC has been shown to be a good indicator of DBP formation potential (Stevens, et al., 1976; Kavanaugh, 1978; Babcock and Singer, 1979; Edzwald et al., 1985). Because TOC concentration has been correlated to overall organic halide formation, the EPA devised its D/DBP Rule to target TOC removal in addition to setting maximum contaminant levels for TTHM and HAA5 concentrations. Specific percent removals of TOC during coagulation are aimed at reducing the public's exposure to other presently unidentified and potentially carcinogenic halogenated organic compounds. Figure 4.7 illustrates the linear relationship between TTHM formation and TOC concentration for the nine waters examined. The R^2 value is 0.95, indicating that TOC is a useful surrogate in predicting TTHM formation for these waters. Figure 4.8 shows the same data except the Tampa raw water data point was removed because it might have skewed the regression in Figure 4.7 due to its high value. The regression equations in Figures 4.7 and 4.8 predict a 26-30 ug/L increase in TTHM concentration for every 1 mg/L increase in TOC concentration for the UFC conditions used here. Literature values for similar correlations range from 45.1 to 78.5 ug TTHM per mg TOC (Edzwald et al., 1985), and have been shown to vary with pH, temperature, contact time and chlorine dose (Kavanaugh, 1978). Therefore, a direct comparison of slopes is not warranted.

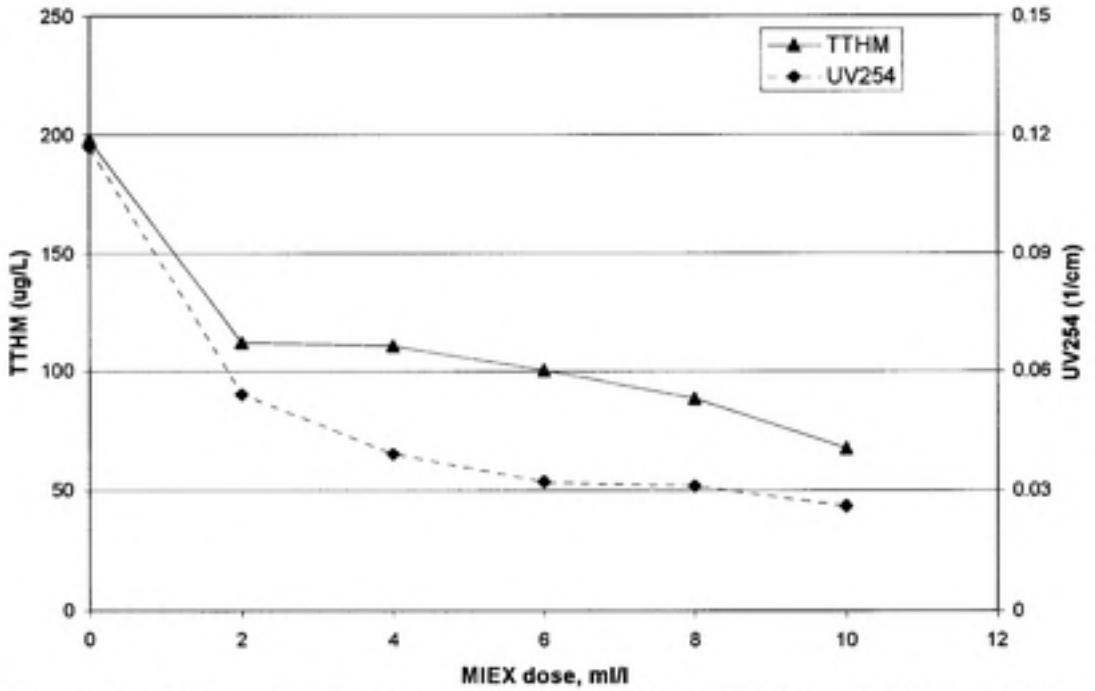

Figure 4.5. UV254 and TTHM concentration as a function of MIEX dose for Sioux Falls, SD.

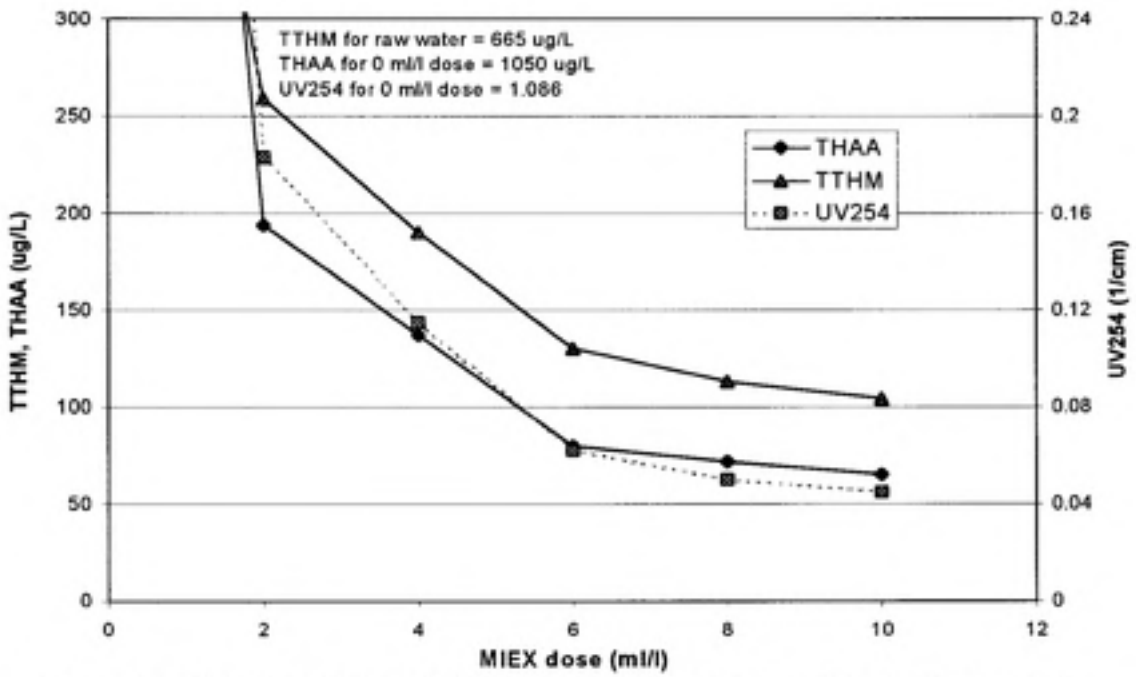

Figure 4.6. UV254, TTHM, and THAA concentration as a function of MIEX dose for Tampa, FL.

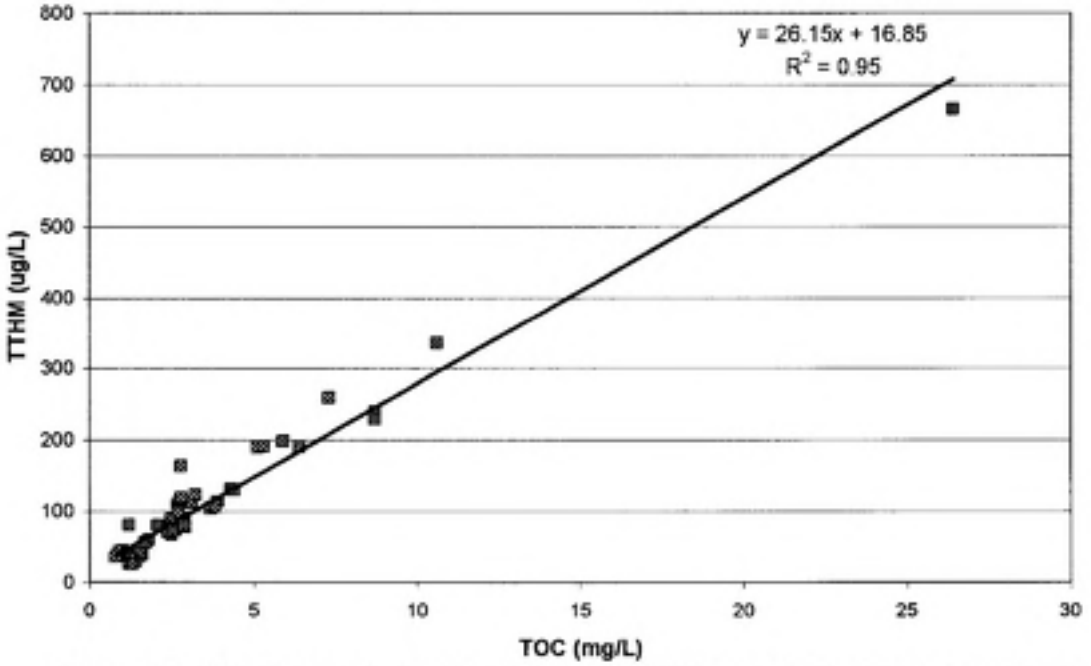

Figure 4.7. TTHM concentration as a function of TOC concentration for raw and MIEX-treated water.

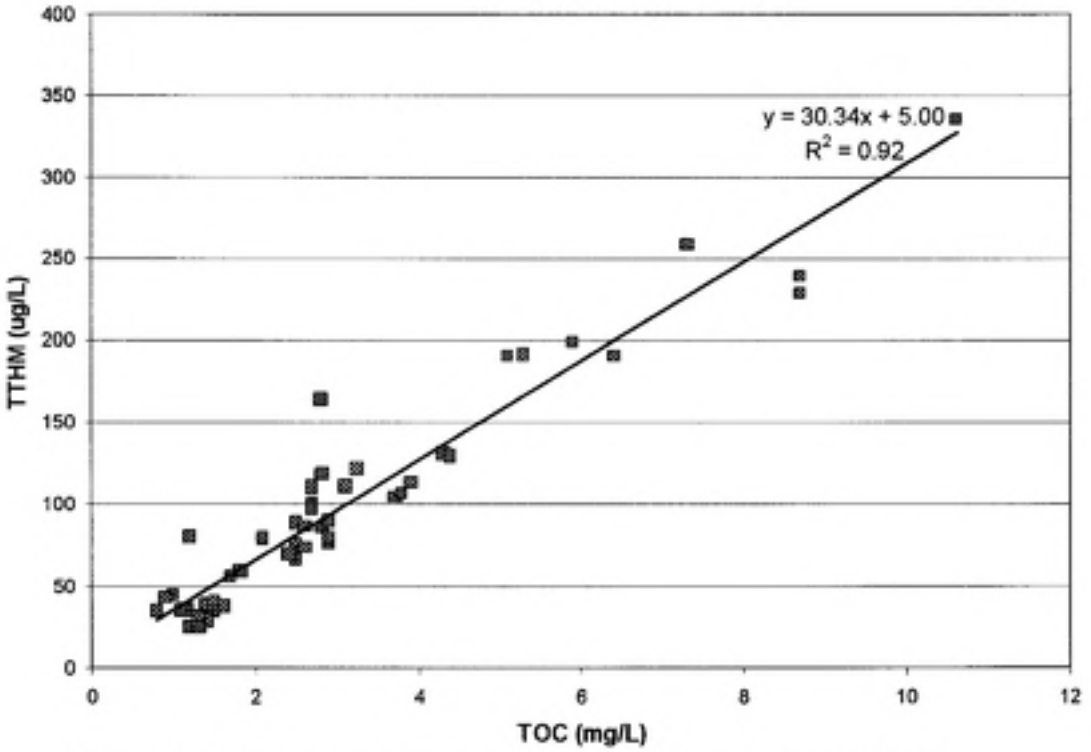

Figure 4.8. Re-plot of data in Figure 4.7, excluding data for Tampa raw water.

4.2. IMPACT OF MIEX ON COAGULATION OF TURBIDITY

MIEX treatment of raw water reduced the amount of alum required for turbidity removal in all nine waters. Figures 4.9-4.11 illustrate the alum dosages required for turbidity removal in water with and without MIEX pre-treatment. MIEX eliminates a significant portion of the coagulant demand in several ways, the most important and obvious of which is a significant reduction in TOC concentration. White, et al., (1997) found a linear correlation between the critical alum dose required to initiate turbidity and TOC removals and the raw water TOC concentration (1997). Indeed, as TOC concentration decreased following MIEX treatment, so did the amount of alum required to coagulate turbidity.

All waters exhibited a reduction in the requisite alum dose for turbidity removal as a result of the removal of organic carbon due to MIEX treatment (see Appendix C). MIEX alone tended to increase the turbidity of the water because of the residual suspended fine resin particles in the water, but subsequent coagulation with alum lowered turbidity to levels comparable with turbidity in raw water treated with alum.

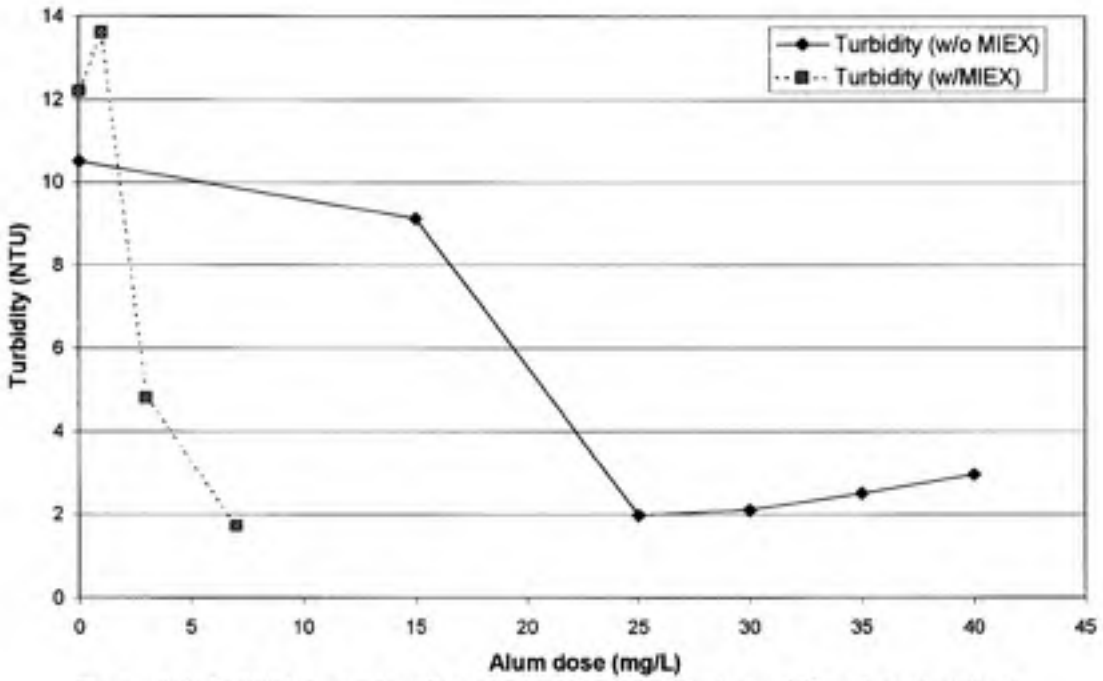

Figure 4.9. Turbidity as a function of alum dose for Durham, NC with and without MIEX pretreatment.

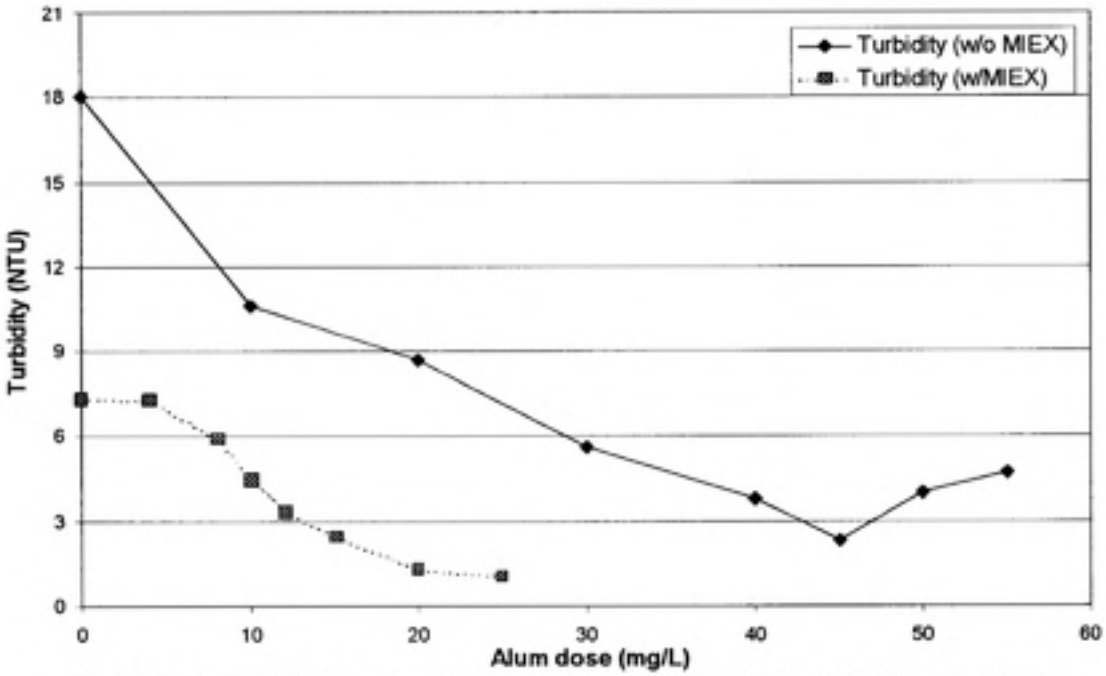

Figure 4.10. Turbidity as a function of alum dose for Sioux Falls, SD with and without MIEX pretreatment.

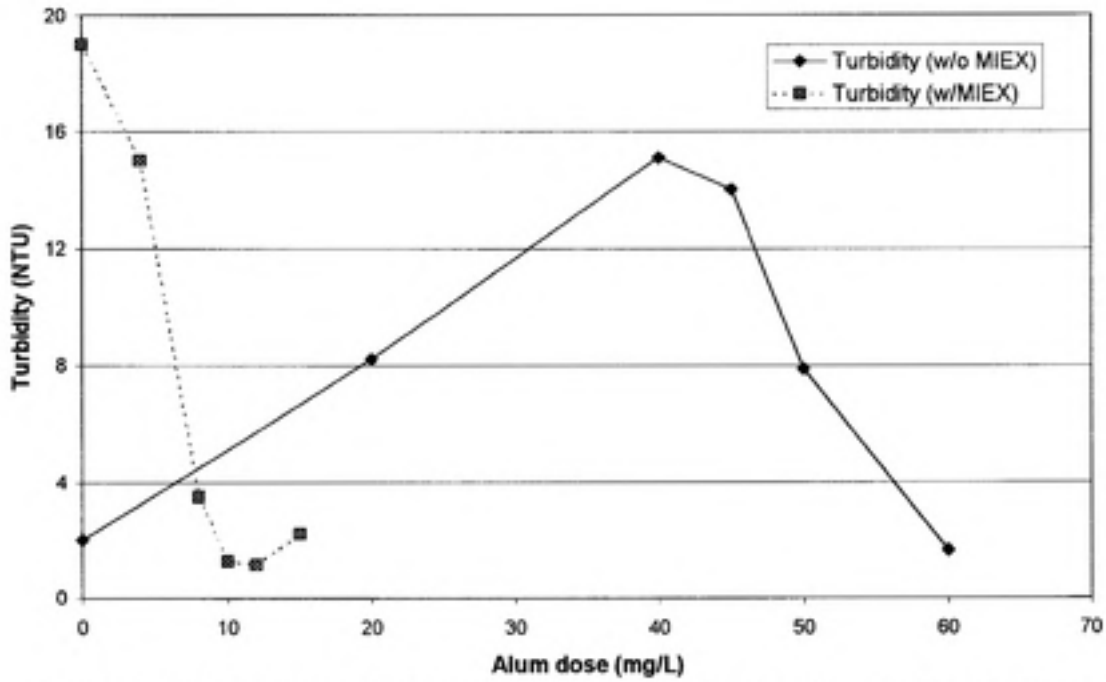

Figure 4.11. Turbidity as a function of alum dosage for Manatee Co., FL with and without MIEX pretreatment.

Figure 4.9 compares the alum dosage required to remove turbidity from raw water and from MIEX-treated water for Durham. Without MIEX treatment, 25 mg/L of alum was required to coagulate this low alkalinity, moderate TOC water (initial TOC = 5.1 mg/L) to achieve a settled water turbidity of less than 2 NTU. The pH of the water before and after coagulation with 25 mg/L of alum was 6.77 and 5.78, respectively. When the raw water was pre-treated with 6 mL/L of MIEX for 20 minutes, the amount of alum required to lower the turbidity to less than 2 NTU was only 7 mg/L. The pH of the water before and after enhanced coagulation with MIEX and alum were 6.60 and 6.25, respectively. Suspended resin following MIEX treatment was observed to contribute to the residual turbidity prior to alum treatment.

Similar findings for Sioux Falls are shown in Figure 4.10. Without MIEX treatment, 45 mg/L of alum was required to lower the turbidity of this high alkalinity, hard water (initial TOC = 8.7 mg/L) to less than 3 NTU. Following treatment with 6 mL/L of MIEX for 30 minutes, the alum demand was reduced to 20 mg/L for coagulation of turbidity. The pH decreased from 8.05 in the raw water to 7.35 after 45 mg/L alum was added. The pH of the water before and after enhanced coagulation with MIEX and alum were 8.04 and 7.75, respectively. The coagulation curve for Sioux Falls raw water differs from the raw water curve for Durham in that there is a steady decrease in turbidity as a function of increasing alum dose for Sioux Falls, whereas for Durham, turbidity did not decrease significantly until between 15 and 25 mg/L of alum was added. This is attributed to the different pH's of the two waters and the corresponding different modes of coagulation.

Figure 4.11 is an illustration of how MIEX treatment reduced coagulant demand for Manatee County, a low alkalinity, high TOC water (initial TOC = 10.6 mg/L). The requisite alum dosage was reduced from 60 mg/L without MIEX treatment to 10 mg/L with MIEX pre-treatment. Although turbidity at 60 mg/L alum is about the same as with no alum treatment, the TOC, DOC, and UV absorbance at 60 mg/L of alum are much lower. The pH of the water before and after coagulation with 60 mg/L of alum was 7.33 and 6.08, respectively. The pH of the water before and after enhanced coagulation with MIEX and alum were 7.14 and 6.92, respectively. Turbidity increased initially upon

alum addition as the dissolved organic carbon in the water was converted to a non-settling particulate form at alum dosages below 40 mg/L. At 40 mg/L alum, coagulation of turbidity was initiated, and at 60 mg/L of alum, turbidity was reduced to less than 2 NTU.

4.3. SUMMARY

TOC, UV254, THM formation potential, and HAA formation potential all decreased as a result of enhanced coagulation with alum, and even greater removals were achieved in waters treated with MIEX and alum, even at lower alum doses. Table 4.2 summarizes the findings for all nine waters in this study.

SUVA values for each utility and the percent removals achieved by alum-, and MIEX and alum-treatment with respect to the raw water values are shown in Table 4.3. This table demonstrates that the percentage of TOC, UV absorbance, and THMFP removed by MIEX and alum-treatment increased with increasing SUVA values. Alum coagulation has been shown in literature to preferentially remove UV absorbing material and THM precursors from raw waters (e.g. Kavanaugh, 1978; Babcock and Singer, 1979; Edzwald et al., 1985). MIEX showed no preference for THM precursors in waters with SUVA values above 2.0 L/mg-m. However, there was a significant preference for THM precursors in waters with SUVA values below 2.0 L/mg-m, as the percent reduction in THMFP exceeded the percent reduction in TOC concentration. MIEX and alum-treatment showed a slight preference for the removal of UV absorbing natural organic material in all waters. Further speculation on the preference of MIEX for aromatic over aliphatic carbon compounds, or hydrophobic over hydrophilic compounds cannot be made without a thorough water quality characteristics analysis of each water.

TTHM concentrations following chlorination of raw, alum-, and MIEX and alum-treated waters for seven of the nine waters studied are compared in Figure 4.12. Manchester and Austin show only a small difference between their raw and alum-coagulated THM formation potentials. Austin and Manchester were both low TOC waters with relatively low SUVAs, and it was therefore difficult to achieve appreciable

Table 4.2. SUMMARY

Utility	Treatment	TOC (mg/L)	UV254 (1/cm)	THMFP (ug/L)	HAAFP (ug/L)
Durham, NC	Raw	5.1	0.175	190	40.3
	30 mg/L Alum	3.1	0.042	84.3	34.2
	6 mL/L MIEX + 7 mg/L Alum	1.2	0.014	36.3	nr
Manatee Co., FL	Raw	10.6	0.477	335	264
	60 mg/L Alum	5.3	0.106	222	125
	8 mL/L MIEX + 10 mg/L Alum	1.4	0.029	nr	nr
Indianapolis, Indiana	Raw	4.6	0.088	nr	59.3
	30 mg/L Alum	3.4	0.068	94.8	38.5
	6 mL/L MIEX + 12 mg/L Alum	nr	0.058	51.7	nr
Hackensack, NJ	Raw	4.3	0.106	131	81.2
	40 mg/L Alum	nr	0.058	84.7	53.9
	4 mL/L MIEX + 12 mg/L Alum	nr	0.02	23.6	nr
Manchester, NH	Raw	2.6	0.03	73.4	31.2
	10 mg/L Alum	2	0.029	58	25.4
	2 mL/L MIEX + 10 mg/L Alum	1.4	0.016	29.4	12.7
Sioux Falls, SD*	Raw	12	0.135	239	113
	45 mg/L Alum	4.9	0.100	167	72.6
	6 mL/L MIEX + 20 mg/L Alum	2.4	0.032	80.8	46.4
Municipal Water District, CA	Raw	2.8	0.081	164	67
	30 mg/L Alum	2	0.048	109	50.7
	6 mL/L MIEX + 10 mg/L Alum	1.1	0.016	35.2	14.2
Austin, TX	Raw	2.8	0.056	119	119
	20 mg/L Alum	2.6	0.041	101	32.5
	6 mL/L MIEX + 10 mg/L Alum	1.3	0.012	25.2	24.0
Tampa, FL	Raw	26.4	1.096	665	833
	150 mg/L Alum	9.3	0.219	196	180
	8 mL/L MIEX + 45 mg/L Alum	2.9	0.047	79.9	nm

nr = not reported because it did not meet our quality assurance criteria

nm = not measured

*Experiments on Sioux Falls were repeated to verify the reproducibility of the experimental procedures. THM formation potential from the second set of experiments was within 10% of the values obtained in the first set of experiments. Data from the first set is reported here.

Table 4.3. SUVA Values for Each Water and Percent Removals Achieved by Alum- and MIEX + Alum-Treatment as Compared to Raw Water

Utility	Raw Water SUVA (L/mg-m)	Treatment	Percent Reduction in TOC	Percent Reduction in UV254	Percent Reduction in THMFP
Manatee Co., FL	4.5	Alum	50%	78%	34%
		MIEX + Alum	87%	94%	89%
Tampa, FL	4.0	Alum	65%	80%	73%
		MIEX + Alum	86%	96%	88%
Durham, NC	3.5	Alum	39%	76%	56%
		MIEX + Alum	76%	92%	81%
Municipal Water District, CA	3.0	Alum	29%	41%	34%
		MIEX + Alum	71%	89%	79%
Hackensack, NJ	2.7	Alum	nr	45%	35%
		MIEX + Alum	nr	81%	82%
Sioux Falls, SD	2.7	Alum	44%	26%	29%
		MIEX + Alum	70%	73%	64%
Austin, TX	2.0	Alum	7%	27%	15%
		MIEX + Alum	54%	79%	79%
Indianapolis, IN	1.9	Alum	26%	23%	nr
		MIEX + Alum	nr	75%	nr
Manchester, NH	1.4	Alum	23%	3%	21%
		MIEX + Alum	46%	53%	60%

nr = not reported due to problems with analytical instrumentation

removal of TOC in these waters, with alum alone. Austin water in particular was difficult to coagulate because it was also a high alkalinity water, and high levels of alkalinity have been known to interfere with effective turbidity and TOC removal by alum coagulation.

A much greater reduction in THM formation potential was observed for the waters treated with MIEX and alum as compared to the raw waters or to the waters treated by alum alone. The vast majority of this reduction was attributable to the MIEX treatment and little additional removal was achieved by the alum. Specific percent removals for each water are shown in Table 4.3. These findings complement the work of

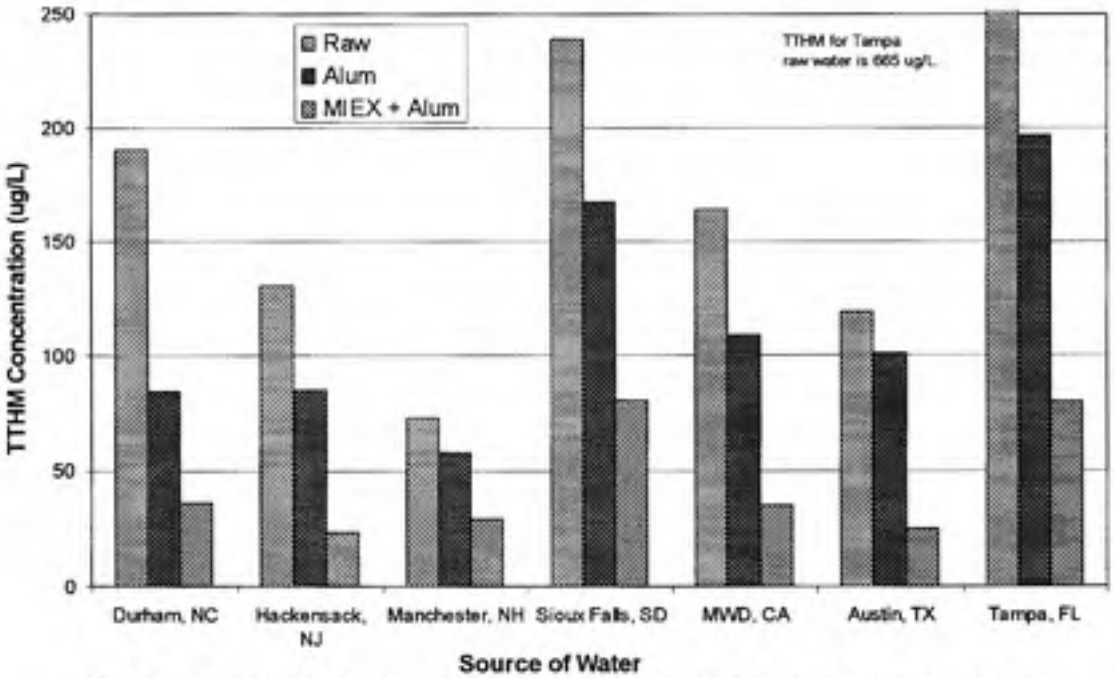

Figure 4.12. TTHM concentration in raw, alum-, and MIEX + alum-treated waters for different source waters.

other researchers who have demonstrated that ion exchange is an effective tool in removing DBP precursors (e.g. Rook and Evans, 1979; Kim and Symons, 1991).

A similar trend was observed for HAA formation potential, as Figure 4.13 illustrates. In this figure, it should be noted that the MIEX-treated sample refers to the MIEX batch-treated water alone, and not the MIEX and alum-treated water. Alum coagulation by itself reduced HAA formation potential, as expected, but the removals by MIEX were much greater, i.e. 59% for Manchester, 59% for Sioux Falls, 79% for MWD, and 80% for Austin.

The relationship between THAA and TTHM formation potentials is shown in Figure 4.14. The correlation implies that THM data, which are much more plentiful in this work, can be extrapolated to suggest that HAA precursors are removed as well as THM precursors despite the more limited set of data.

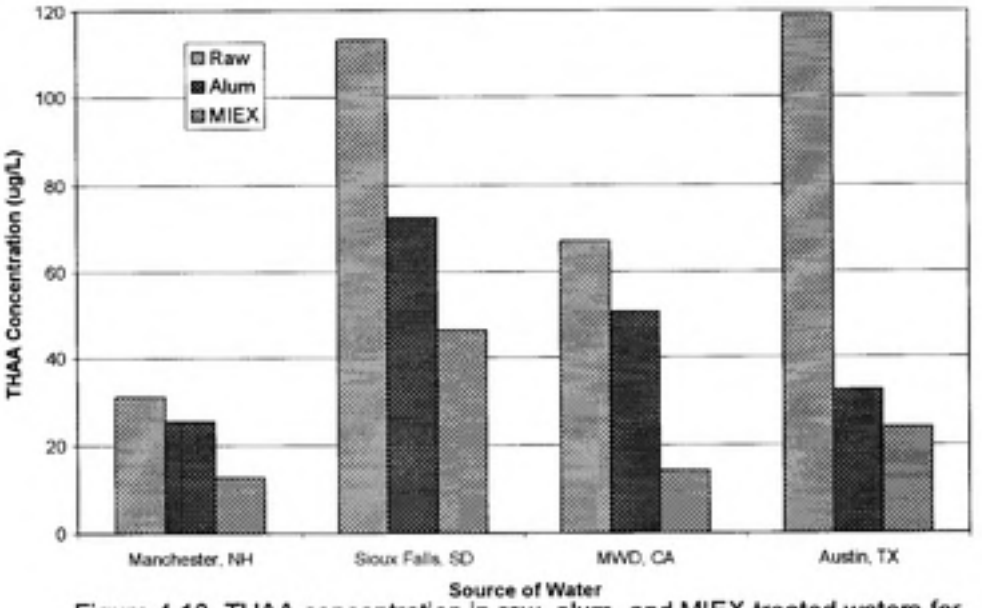

Figure 4.13. THAA concentration in raw, alum- and MIEX-treated waters for different source waters.

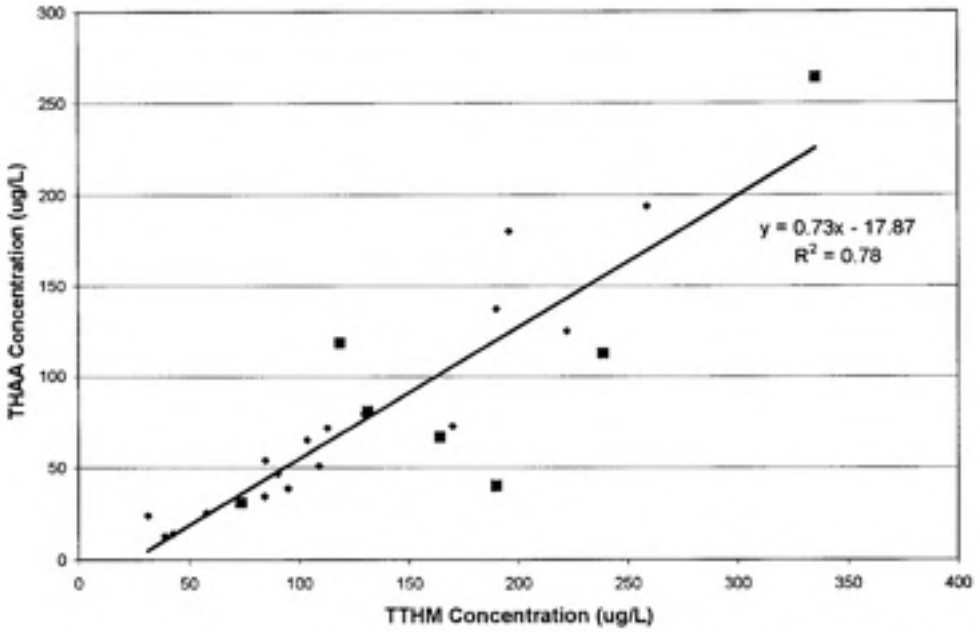

Figure 4.14. Relationship between THAA and TTHM formation for raw, alum- and MIEX-treated waters, excluding Tampa raw water data point. Large squares denote raw waters.

4.4. REMOVAL OF BROMIDE BY MIEX

Table 4.4 shows that MIEX resin was capable of removing bromide from those waters that were analyzed for bromide before and after MIEX treatment, and that bromide removal decreased as alkalinity increased. Since MIEX contains a strong-base anion exchange resin, high alkalinity waters offer more competition in ion exchange applications because of the high concentration of bicarbonate ions competing with bromide for the ion exchange sites.

Table 4.4. Removal of Bromide by MIEX

Utility	Treatment	Br- (ug/L)	alkalinity (mg/L as CaCO3)
Indianapolis	Raw	38.1	155
	Batch treated	40.8	
Tampa	Raw	94.5	91
	Batch treated	54.1	
Manatee	Raw	163	20
	Batch treated	<10	
Manchester	Raw	13.7	4
	Batch treated	<10	

Bromide has been shown to affect the concentration and speciation of THMs and HAAs (e.g. Stevens, et al., 1976; Pourmoghaddas, et al., 1993; Cowman and Singer, 1995). The formation of dichloroacetic acid, trichloroacetic acid, and chloroform has been shown to decrease as the concentration of bromide increases (Rook, 1978; Pourmoghaddas, et al., 1993; Cowman and Singer, 1995). When raw water is coagulated with alum, the concentration of TOC decreases, but the bromide concentration tends to remain constant. Hence, the ratio of bromide ion concentration to TOC concentration increases, and therefore more brominated THMs and HAAs are produced upon subsequent chlorination. This can be seen in Figure 4.15 as a decrease in the percent of TTHM due to chloroform in all of the alum-treated samples. This same phenomenon has been demonstrated following GAC and membrane treatment for TOC (NOM) removal. Figure 4.15 also shows the percent of TTHM attributable to chloroform for the MIEX

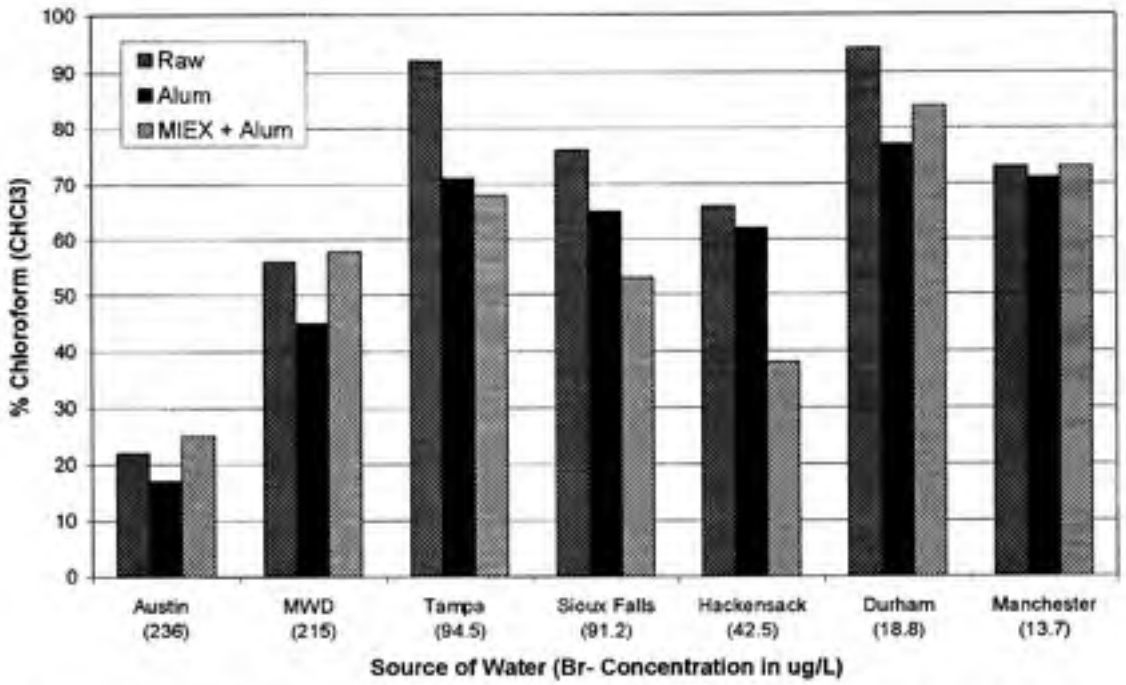

Figure 4.15. Percent TTHM due to chloroform in raw, alum-, and MIEX + alum-treated waters.

and alum-treated samples. Austin and MWD are two low TOC waters that had low chlorine demands and high bromide concentrations in the raw water. They also exhibited lower percent TOC removal than the higher TOC waters but achieved significant bromide removals as a result of MIEX pre-treatment. Hence they had lower bromide to TOC ratios than the other waters. The decrease in the bromide to TOC ratio as a result of MIEX and alum treatment favored the formation of more chloroform than brominated THM species compared to the alum-treated waters from the same source. Accordingly, the percentage of TTHM as chloroform increased for the MIEX and alum-treated samples in these two waters. Manchester and Durham also showed an increase in the percentage of TTHM as chloroform in the MIEX and alum-treated water as compared to the alum-treated water. Interestingly, Durham and Manchester had very low bromide concentrations, 18.8 ug/L and 13.7 ug/L, respectively. If all of the bromide in these waters were removed, which is likely because they had extremely low alkalinities (20 mg/L and 4 mg/L, respectively), the bromide to TOC ratios in these waters would be extremely low as well, accounting for the speciation shift towards more choloform. The

other waters did not show the same trend, perhaps because the bromide to TOC ratio increased due to proportionally larger percent TOC removals with respect to the raw water (e.g. Tampa, Sioux Falls).

Bromide removal with MIEX was an unexpected outcome of this investigation as the objectives of the project were not to determine the effects of MIEX on bromide removal or on DBP speciation. It is an interesting finding and one worthy of further study, as brominated disinfection by-products are believed to be more harmful to public health than their chlorinated counterparts.

4.5. COST

A crude cost model was created to compare the cost of adding a MIEX treatment train onto an existing water treatment plant and the corresponding cost savings due to a reduction of the requisite alum dosage for the removal of turbidity. Costs were computed for a 1, 10, and 100 MGD plant to compare economies of scale. Appendix D contains a list of assumptions used in the analysis and Table 4.5 shows how the costs were broken down into capital and operating expenses. The operating costs for a MIEX system included the cost of power, resin, regenerant, and disposal of waste regenerant. These costs were obtained from Orica, the resin manufacturer (Bourke, 2000). A high and a low estimate for operating costs associated with MIEX was generated based on a range of estimates and disposal options. These values were used to band the expected cost of a MIEX system. Capital costs for a MIEX system included the cost of the regeneration system, mixing tank, and sedimentation tank. The cost of the regeneration system was obtained from EPA's Estimating Water Treatment Costs publication (USEPA, 1979). The cost of this system was brought up to date using a costing index from Statistical Abstracts of the United States (U.S. Census Bureau, 1999). The cost of the mixing tank and sedimentation tank was obtained from Camp Dresser and McKee, an environmental engineering consulting firm specializing in water treatment plant design (Dowbiggin, 2000). Operating costs for alum included the cost of the alum and the cost of sludge disposal to sanitary sewers. Estimating the cost of alum was a straightforward calculation described in Appendix D. The cost of sludge disposal required first calculating the mass

Table 4.5. Cost Analysis Worksheet

Parameter	Plant Uses MIEX Plant Size (MGD) 1	10	100	Conventional Plant Plant Size (MGD) 1	10	100
Operating costs for MIEX						
operating costs (power, resin, regenerant)						
high estimate ($/d)	200	2000	20000			
low estimate ($/d)	140	1400	14000			
cost of miex based on this estimate (high) ($/d)	160	1600	16000			
cost of miex based on this estimate (low) ($/d)	112	1120	11200			
disposal of waste regenerant ($/d) (high)	40	400	4000			
disposal of waste regenerant ($/d) (low)	0	0	0			
Capital Costs for MIEX						
Cost of regeneration system in 1979 ($ million)	0.2	0.7	5			
GDP index for 1979 (1992 is base year = 100)	55.2	55.2	55.2			
GDP index for 1998 (2000 data not available)	112.7	112.7	112.7			
Cost of regeneration system in 1998 ($)	0.41	1.43	10.21			
Cost of mixing tank ($ million)	0.1	0.4	1.6			
Cost of sedimentation tank ($ million)	0.5	2.5	12			
Operating Costs for Alum						
for x mg/L alum a day, cost ($/d) is computed:						
8.34*(dose mg/L)*(size of plant MGD)*100%/ (8.5%)*cost ($/lb)						
mg/L alum used	10	10	10	60	60	60
cost of alum ($/lb)	0.07	0.07	0.07	0.07	0.07	0.07
cost of alum ($/d)	68.7	686.8	6868.2	412.1	4120.9	41209.4
mass of sludge produced (lb/d)	62	617	6172	245	2452	24520
volume of sludge produced (m^3/yr)	146	1456	14564	579	5786	57864
volume of sludge (MG/yr)	0.04	0.4	3.8	0.15	1.5	15.3
cost of disposal to sanitary sewers ($/yr)	113	1188	11934	468	4738	47433
Capital Costs for Alum						
none, the process is already installed						
TOTAL CAPITAL ($ million)	1.01	4.33	23.81	0.00	0.00	0.00
TOTAL OPERATING COSTS ($ million/yr) (high	0.113	1.128	11.279	0.151	1.509	15.089
TOTAL OPERATING COSTS ($ million/yr) (low)	0.076	0.763	7.629	0.151	1.509	15.089
Present equivalent cost for the system = capital costs + operating costs (P/A,i,n)						
interest rate (%)	8	8	8	8	8	8
life cycle (years)	20	20	20	20	20	20
(P/A,i,n)	9.8181	9.8181	9.8181	9.8181	9.8181	9.8181
high cost estimate	2.12	15.4	135	1.48	14.8	148
low cost estimate	1.76	11.8	99	1.48	14.8	148
maximum savings (millions of $)	-0.28	3.0	14			

of sludge produced, then, translating this into a volume of sludge. EPA's Estimating Water Treatment Costs publication (USEPA, 1979) and the costing index were used to calculate the annual cost of disposal to sanitary sewers. There were no capital costs associated with alum treatment because the coagulation process was assumed to be already in place.

Total capital and operating expenses are summarized near the bottom of Table 4.5. The present value of the operating costs was calculated assuming an 8% interest rate and a 20-year life cycle. The present value of the operating costs was added to the capital costs for the MIEX system to compare the present value cost of adding a MIEX treatment train onto an existing water treatment plant with the operating costs that would be incurred if conventional alum treatment continued to be the primary form of organic carbon and turbidity removal. The maximum savings are the difference between the conventional alum treatment plan and the low estimate for a MIEX system. A positive number indicates the maximum amount of money that could be saved by installing a MIEX system, whereas a negative number indicates that MIEX is not likely to be cost-effective at this scale.

The above analyses were computed for a fixed interest rate (8%) and life cycle (20 years). Changing the interest rate or number of years in the life cycle can have a significant effect on determining if MIEX technology is cost-effective. Figure 4.16 shows the present value of the life cycle costs for a 10 MGD plant as a function of the number of years in the life cycle for an 8% interest rate. MIEX enters the cost-effective range after approximately an 8-year life cycle. If this plant were to invest in MIEX technology, it could pay for itself in as little as eight years. Appendix E shows the effect of changing the number of years in the life cycle on the present value cost for the MIEX and conventional systems for a 1 and 100 MGD plant. Appendix E also shows the effect of changing the interest rate for a constant life cycle (20 years) on the present value cost for the MIEX and conventional systems for a 1, 10, and 100 MGD plant. Table 4.5, Figure 4.16 and the figures in Appendix E, for illustative purposes, assume 10 mg/L of

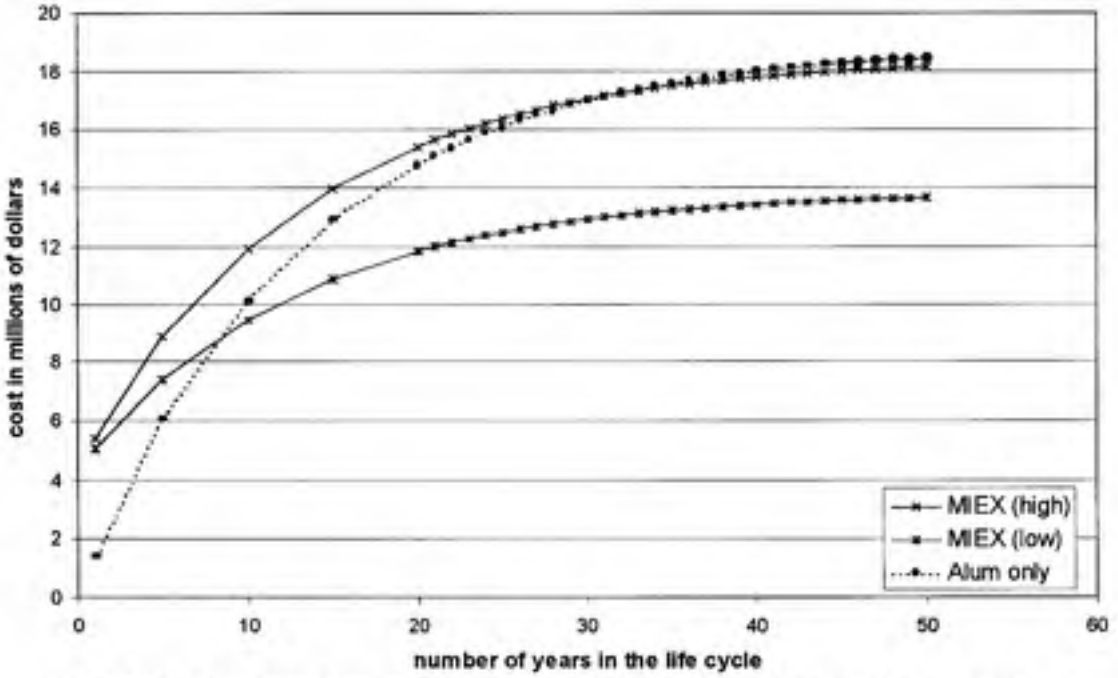

Figure 4.16. The present value of the life cycle costs for a 10 MGD plant as a function of the number of years in the life cycle (interest rate = 8%).

alum is required with MIEX treatment and 60 mg/L of alum is required without MIEX treatment.

Four possible scenarios for alum dose requirements and what it would cost to build and operate a facility for each scenario over a 20-year life cycle assuming an 8% interest rate are compared in Table 4.6. Alum doses for each scenario were based on alum requirments to achieve effective turbidity removals for four of the waters examined in this study. In the first scenario, based on the Hackensack results, 12 mg/L of alum is required with MIEX treatment and 40 mg/L of alum is required without MIEX treatment. The MIEX process is not cost-effective on any scale. Scenario 2 (Manatee Co.) may be cost-effective at the 10 MGD scale and above. This means that somewhere between 10 and 100 MGD, MIEX treatment becomes cost-effective for a Manatee-type water. Under scenario 3, MIEX is not cost-effective at any scale. This example was chosen based on Sioux Falls, a high alkalinity, high TOC water. It is known that high alkalinity waters are difficult to coagulate, and this was shown by the high coagulant demand, even in the MIEX-treated water. Scenario 4, based on the Tampa results, is cost-effective on all

scales, even with the high coagulant demand in the MIEX-treated water. These scenarios demonstrate that the amount of alum saved when MIEX technology is used is very important in determining cost-effectiveness.

Table 4.6. FOUR SCENARIOS FOR ALUM DOSE REQUIREMENTS (BASED ON WATERS IN THIS STUDY)

Present Value of Costs over 20 years, interest rate = 8% (millions of dollars)	Plant Size (MGD) 1	10	100
Scenario 1: Hackensack, NJ			
ALUM: 12 mg/L (w/MIEX), 40 mg/L (w/o MIEX)			
with MIEX	1.8-2.2	12.3-15.9	104-139
without MIEX	1.0	9.9	98.8
Scenario 2: Manatee Co., FL			
ALUM: 10 mg/L (w/MIEX), 60 mg/L (w/o MIEX)			
with MIEX	1.8-2.1	11.8-15.4	98.7-135
without MIEX	1.5	14.8	148
Scenario 3: Sioux Falls, SD			
ALUM: 20 mg/L (w/MIEX), 45 mg/L (w/o MIEX)			
with MIEX	2.0-2.4	14.3-17.9	123-159
without MIEX	1.1	11.1	111
Scenario 4: Tampa, FL			
ALUM: 45 mg/L (w/MIEX), 150 mg/L (w/o MIEX)			
with MIEX	2.6-3.0	20.5-24.0	185-221

One limitation of this cost analysis is that it used turbidity removal as the performance criterion and does not consider the fact that MIEX was capable of achieving reductions in TOC and THM concentrations that alum treatment alone may never be able to achieve. Thus, this cost analysis tends to underestimate the value of MIEX.

In summary, the cost-effectiveness of MIEX will depend on the capacity of the water treatment plant, the magnitude of the reduction in alum dosage, the corresponding requisite alum dose, and the significant degree to which use of MIEX for DBP control is able to obviate the need for other more expensive technologies such as ozone, GAC, and membranes. Interest rates and the life span of the investment will also be factors, as well

as the cost of MIEX regeneration and disposal of the waste regenerant stream. The cost analysis performed here should be considered only as preliminary.

CHAPTER 5
CONCLUSIONS

5.1. CONCLUSIONS

MIEX technology represents another tool for potential use by water utilities to enhance the removal of natural organic material (DBP precursors) in drinking water beyond that achievable by coagulation alone. The conclusions of this investigation are as follows:

- Enhanced coagulation with MIEX was found to be very effective for removing THM precursors from the nine waters examined. THM formation potential was reduced by more than 60% in all waters examined.
- Residual TOC concentration, UV absorbance, and THM formation potential were all substantially lower as a result of MIEX and alum treatment as compared to alum coagulation alone.
- HAA formation potential was substantially lower as a result of MIEX treatment as compared to alum coagulation.
- MIEX was capable of removing bromide from the surface waters examined; bromide removal decreased as alkalinity increased.
- MIEX substantially lowered the coagulant demand of the treated water.
- The cost-effectiveness of adding a MIEX treatment train onto an existing surface water treatment plant was found to be a function of the size of the water treatment plant, the magnitude of the reduction in alum dose, and the significant degree to which use of MIEX for DBP control is able to obviate the need for other more expensive technologies such as ozone, GAC, and membranes. The interest rate and number of years in the life cycle used to compute the present value of the operating costs were also shown to be important factors in determining if MIEX would be a cost-effective technology to add to a conventional alum coagulation plant.

5.2. RECOMMENDATIONS

Having shown that MIEX is capable of removing NOM from natural waters in a bench-scale batch treatment mode, the next step is to demonstrate that MIEX performs

effectively in continuous-flow reactors by performing pilot plant tests. Because virgin MIEX was used in this study, regeneration efficiencies and resin effectiveness after multiple recycle were not considered. In a pilot plant study, these parameters could be quantified and the results used to determine its cost-effectiveness for a specific plant.

Another recommendation is to further examine the extent of bromide removal with MIEX and to determine what other water quality characteristics affect bromide removal efficiency in addition to alkalinity.

It would also be interesting to examine the nature of TOC removal by MIEX by tracking either SUVA or hydrophobic and hydrophilic dissolved organic carbon concentrations as a function of increasing MIEX dosage. These experiments could determine if MIEX preferentially removes either hydrophobic or hydrophilic NOM.

Finally, future researchers may want to include TOX sampling in their chlorination studies to verify that reductions in TOX formation are proportional to decreases in THM and HAA concentration. This would give utilities greater confidence that MIEX was successfully meeting the objectives of the Stage I D/DBP Rule.

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APPENDIX A

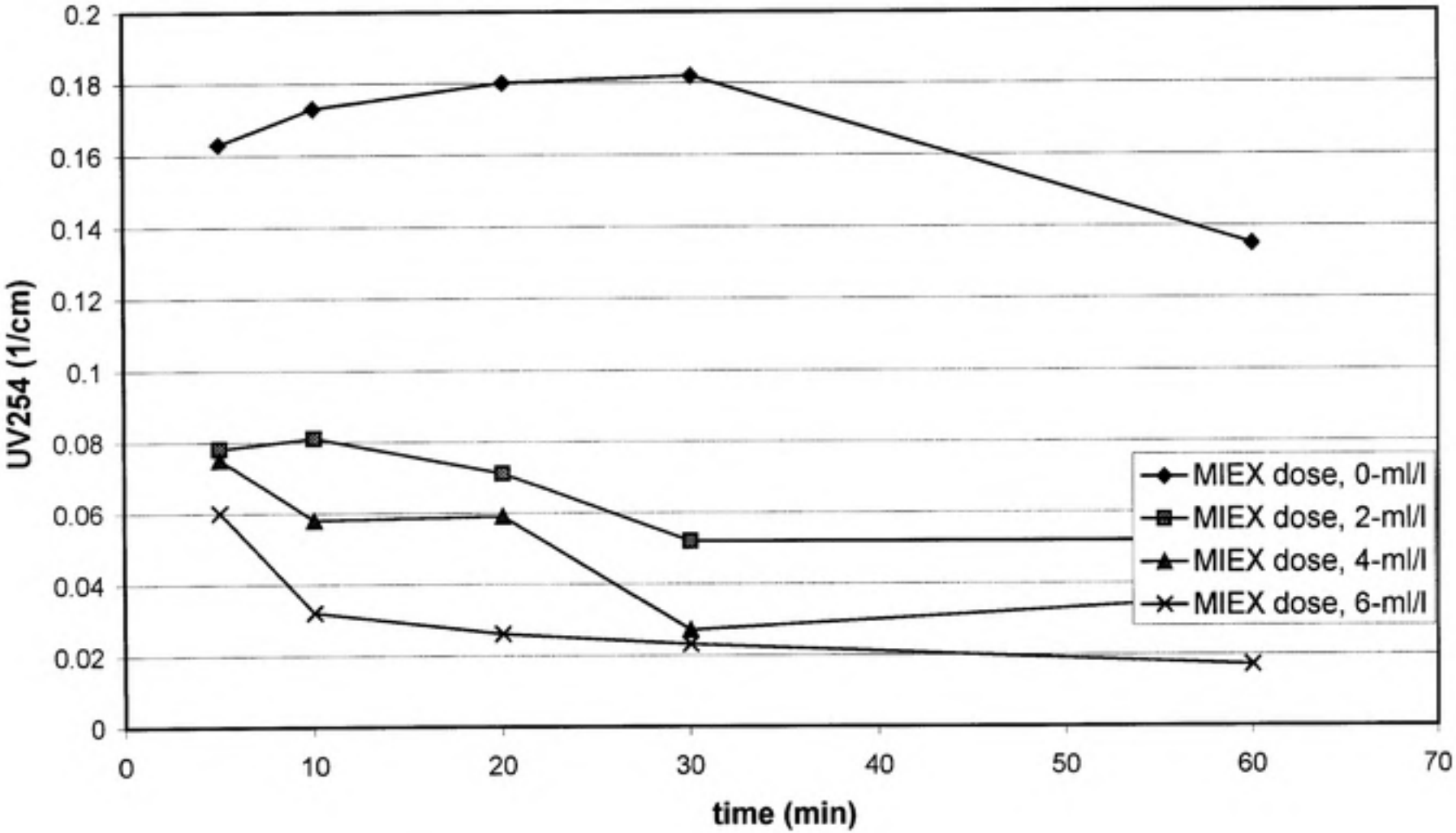

Figure A.1. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From Durham, North Carolina

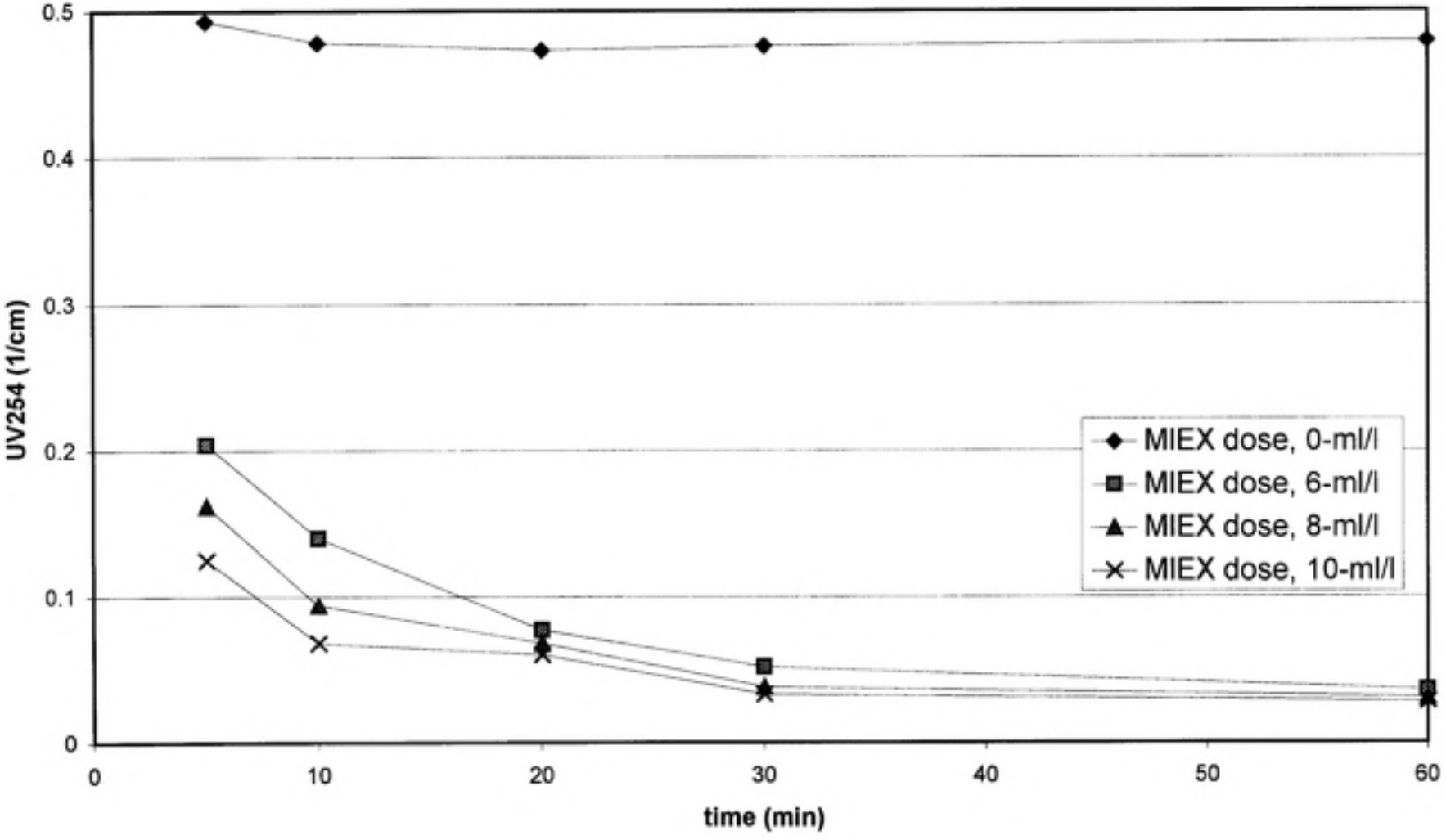

Figure A.2. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From Manatee Co., Florida

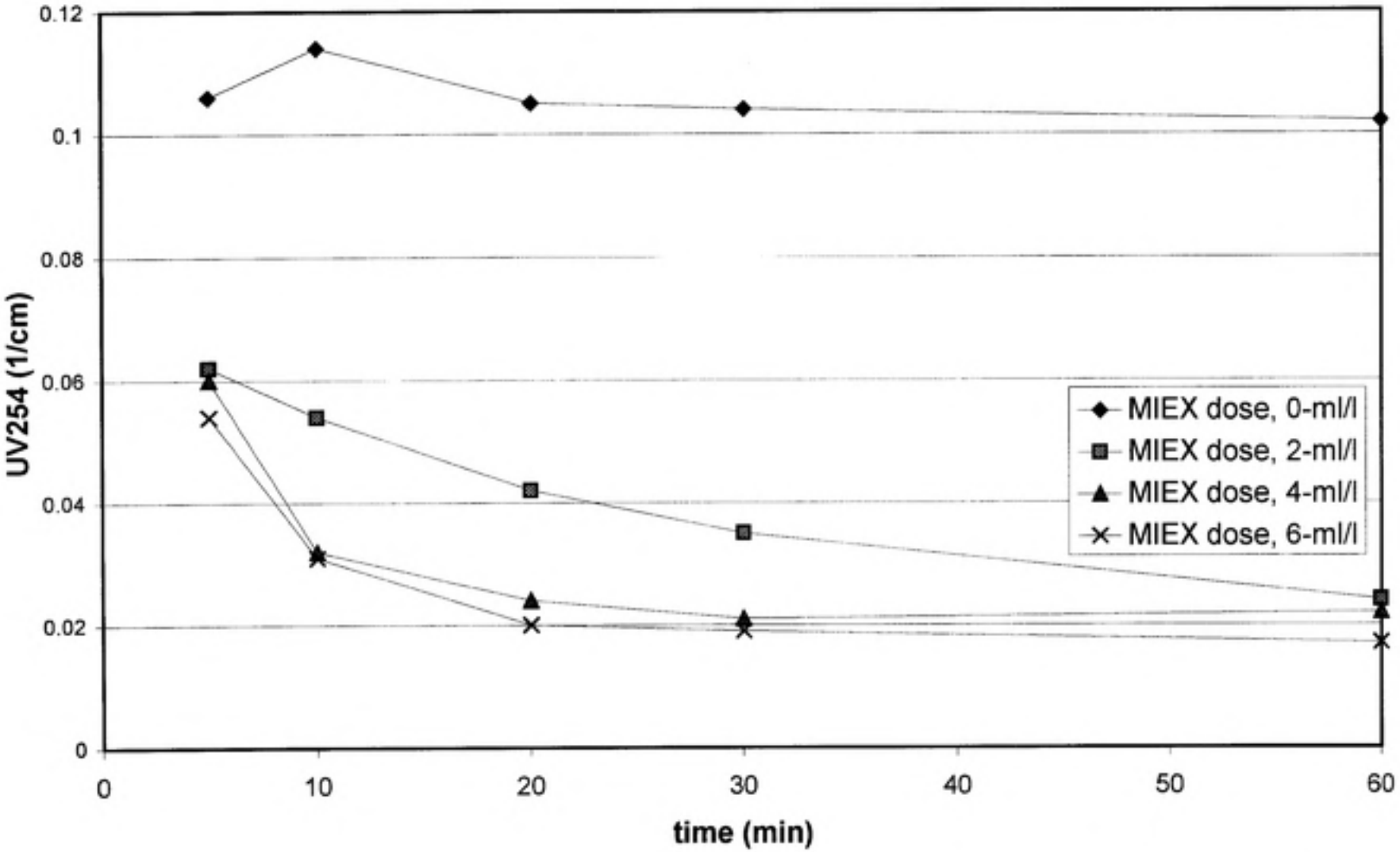

Figure A.3. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From Hackensack, New Jersey

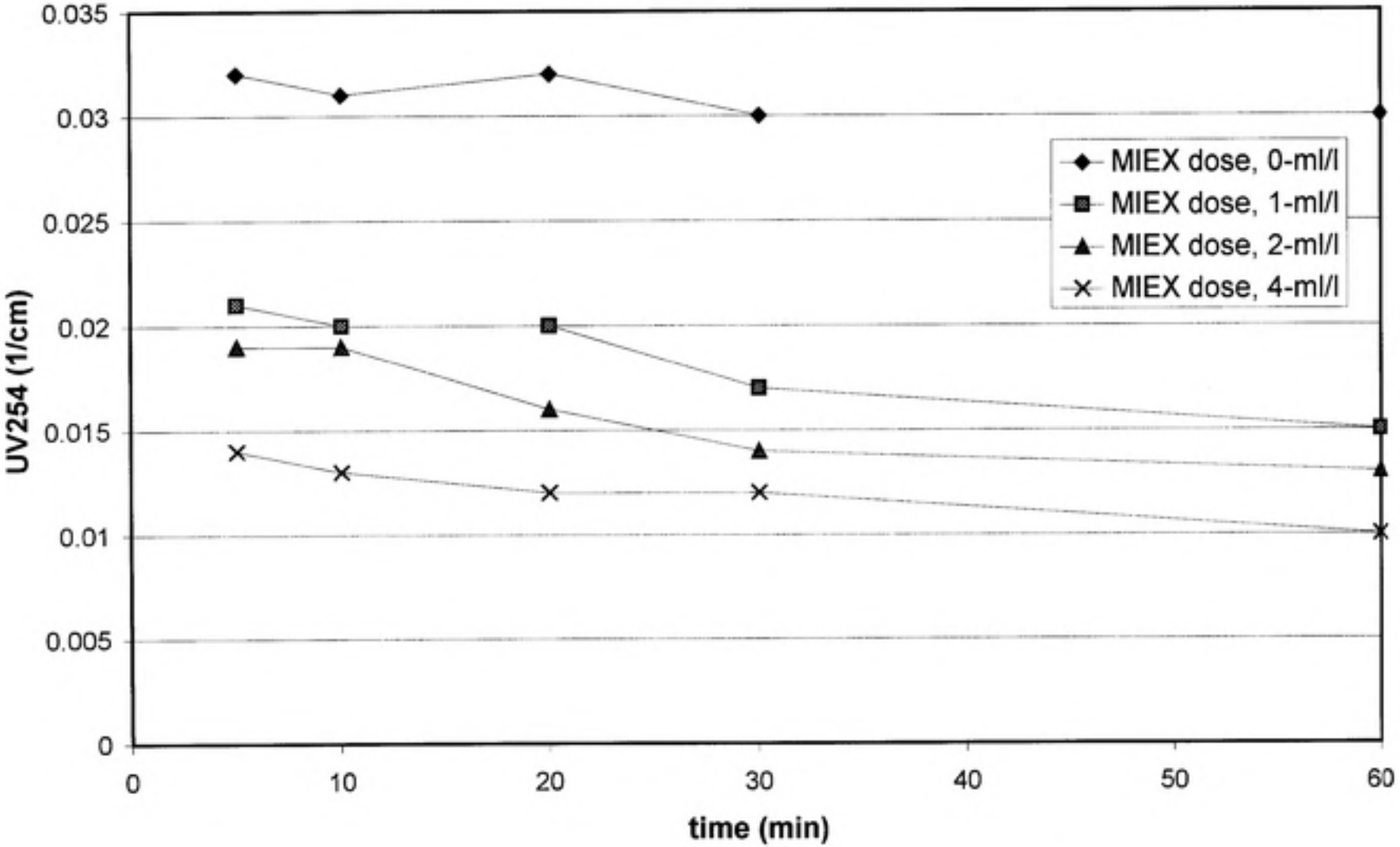

Figure A.4. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From Manchester, New Hampshire

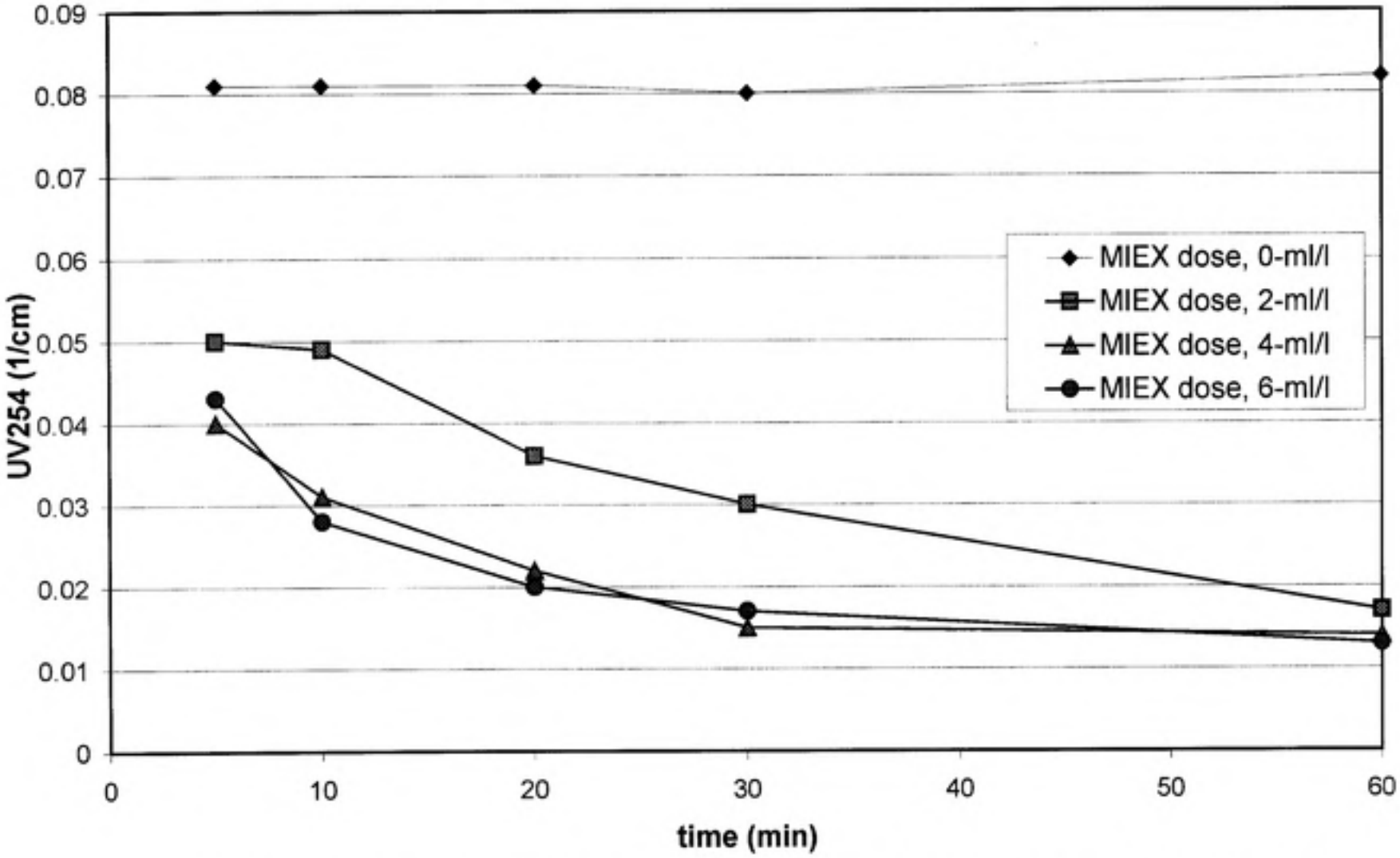

Figure A.5. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From MWD, California

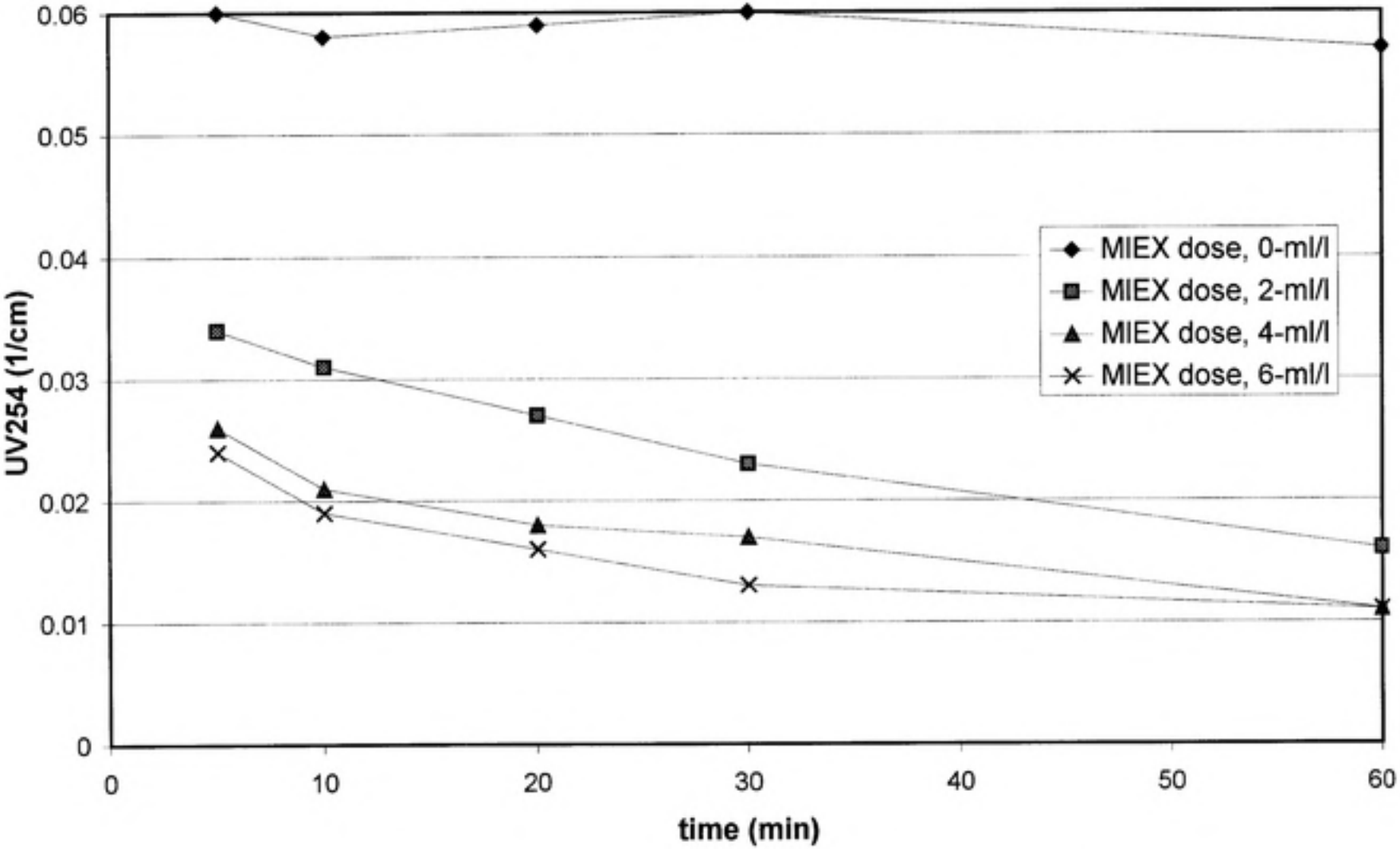

Figure A.6. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water From Austin, Texas

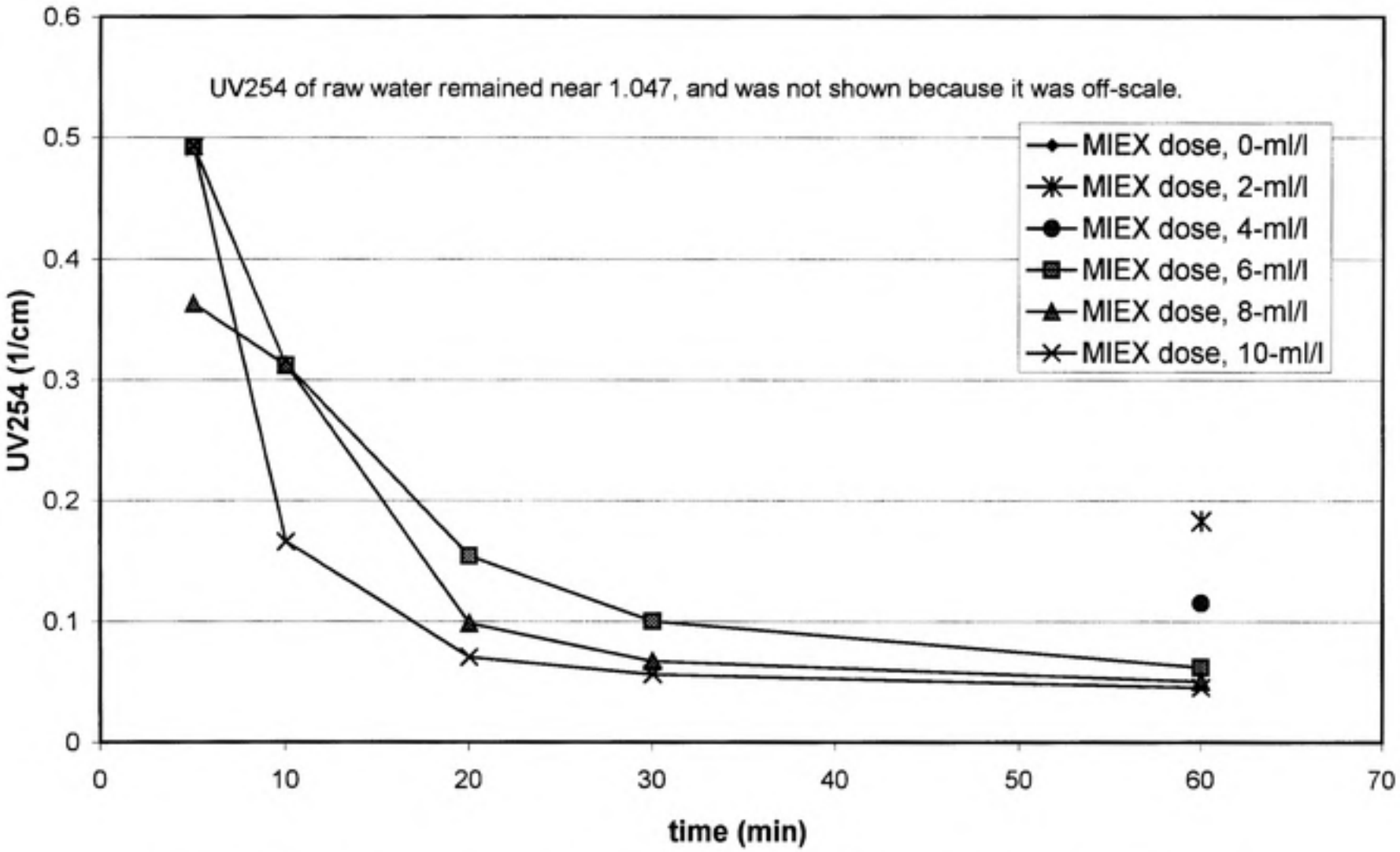

Figure A.7. Ultraviolet Absorbance as a Function of Mixing Time for Different MIEX Doses Added to Raw Water from Tampa, Florida

APPENDIX B

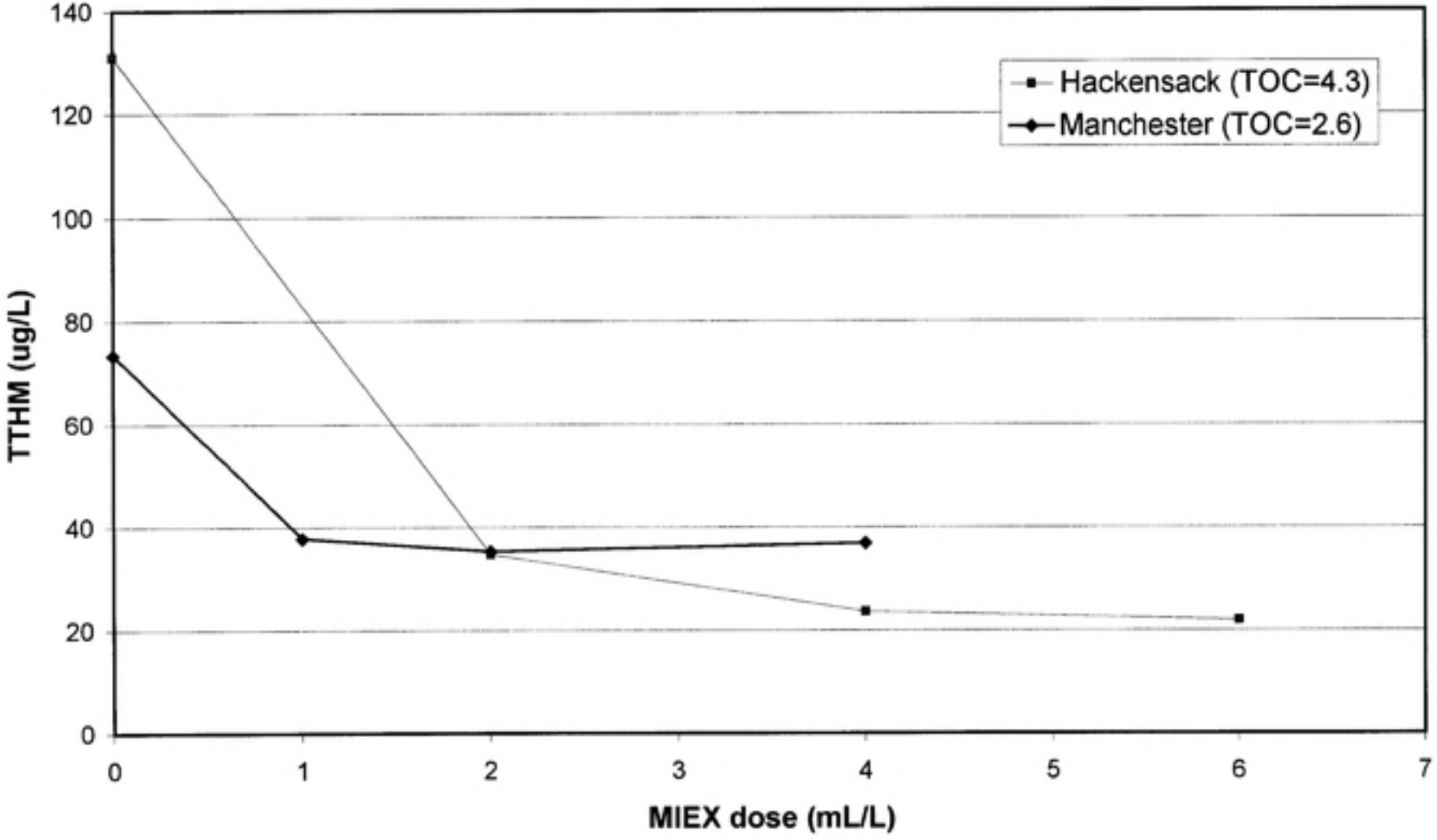

Figure B.1. TTHM Concentration as a Function of Increasing MIEX Dose for Hackensack and Manchester Raw Waters

APPENDIX C

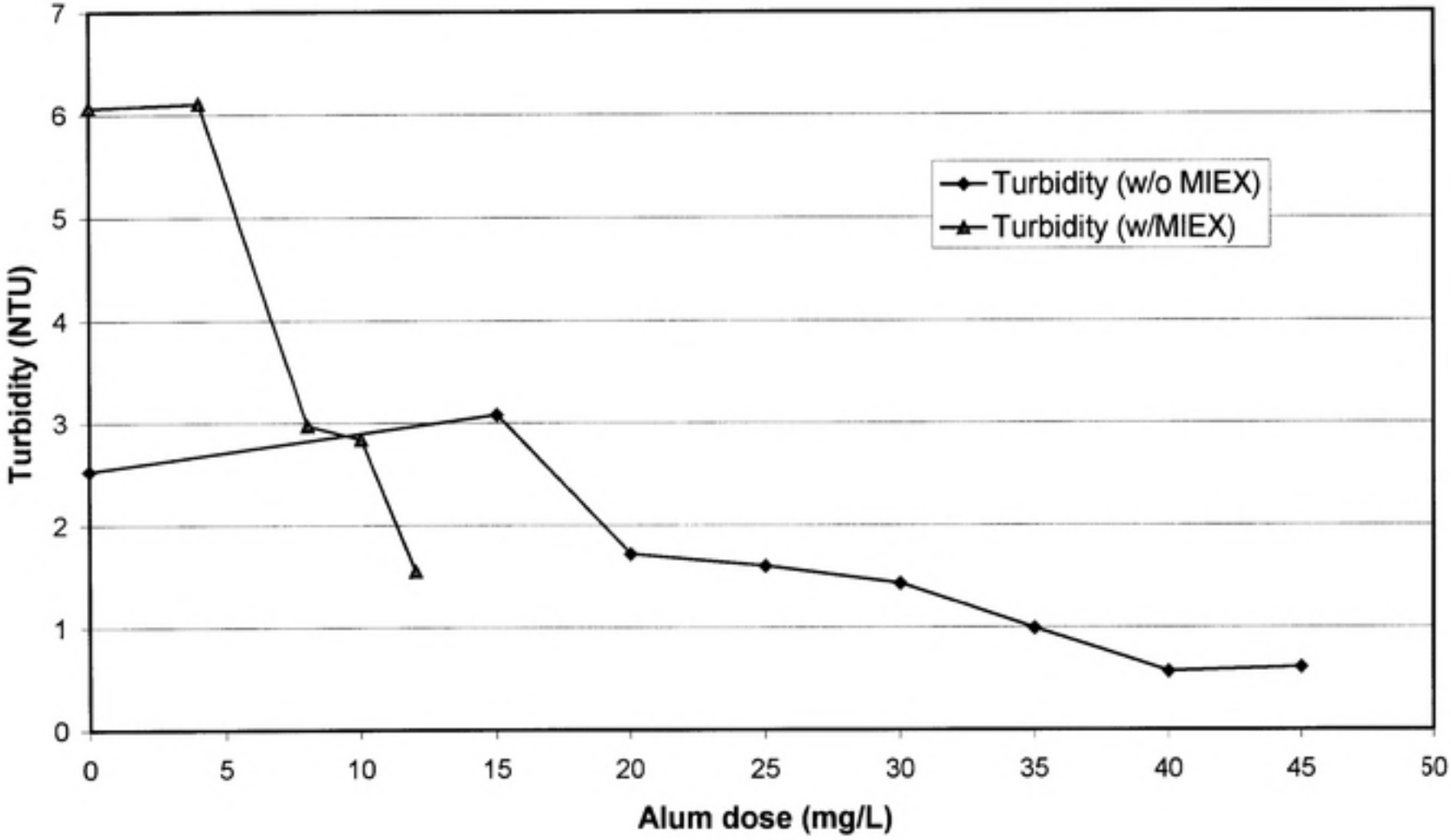

Figure C.1. Turbidity as a Function of Alum Dose for Indianapolis, IN with and without MIEX Pretreatment

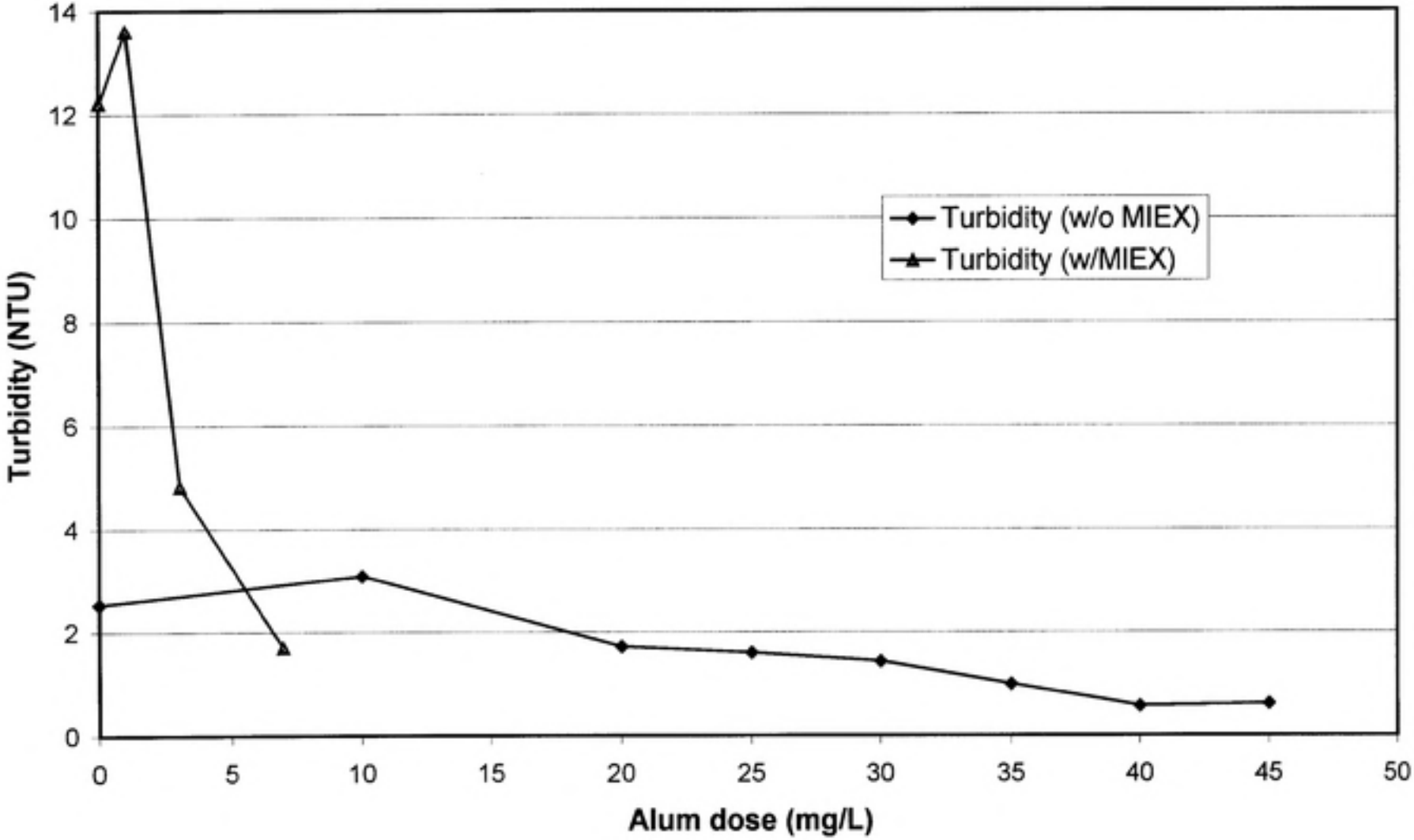

Figure C.2. Turbidity as a Function of Alum Dose for Hackensack, NJ with and without MIEX Pretreatment

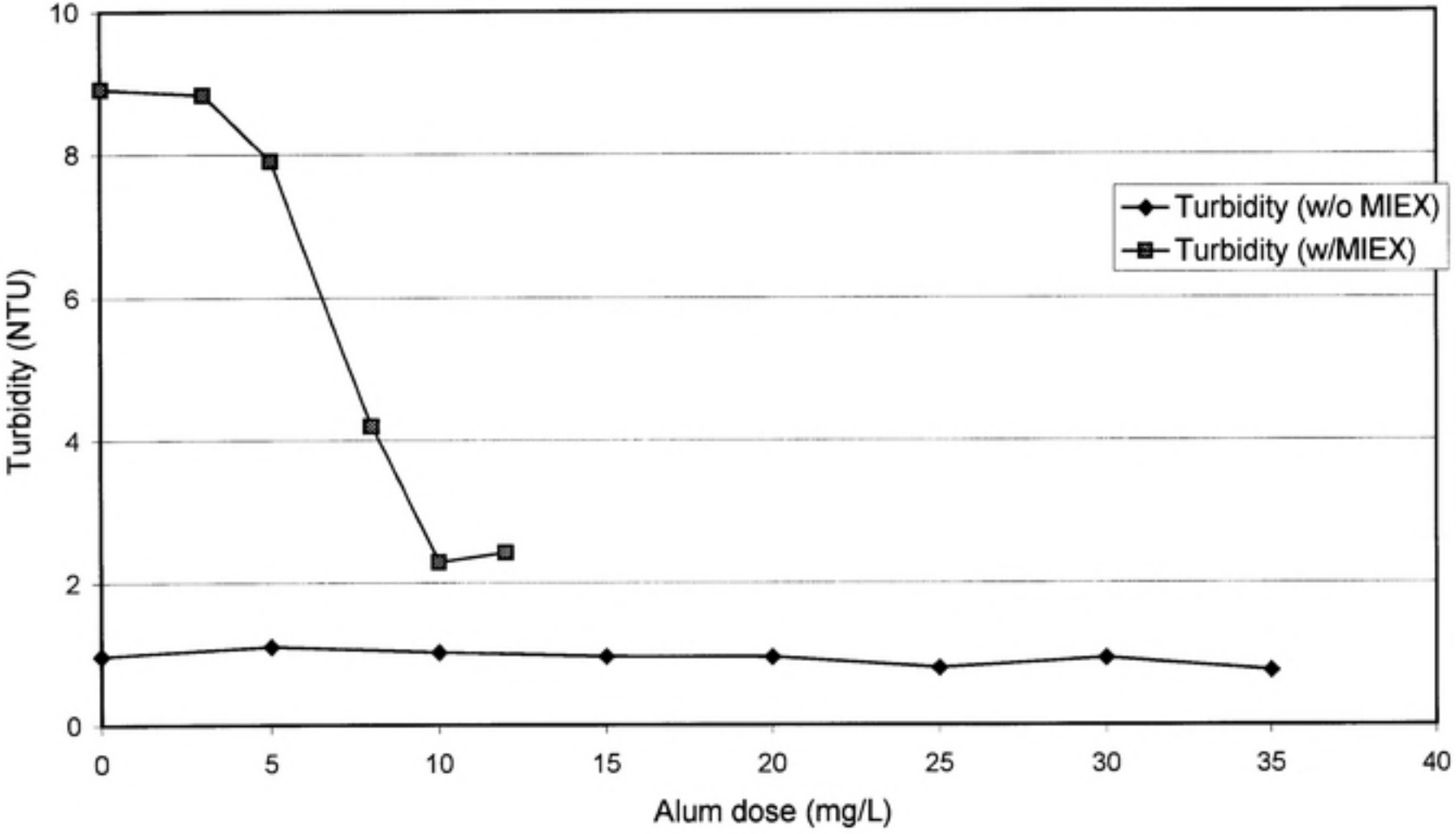

Figure C.3. Turbidity as a Function of Alum Dose for Manchester, NH with and without MIEX Pretreatment

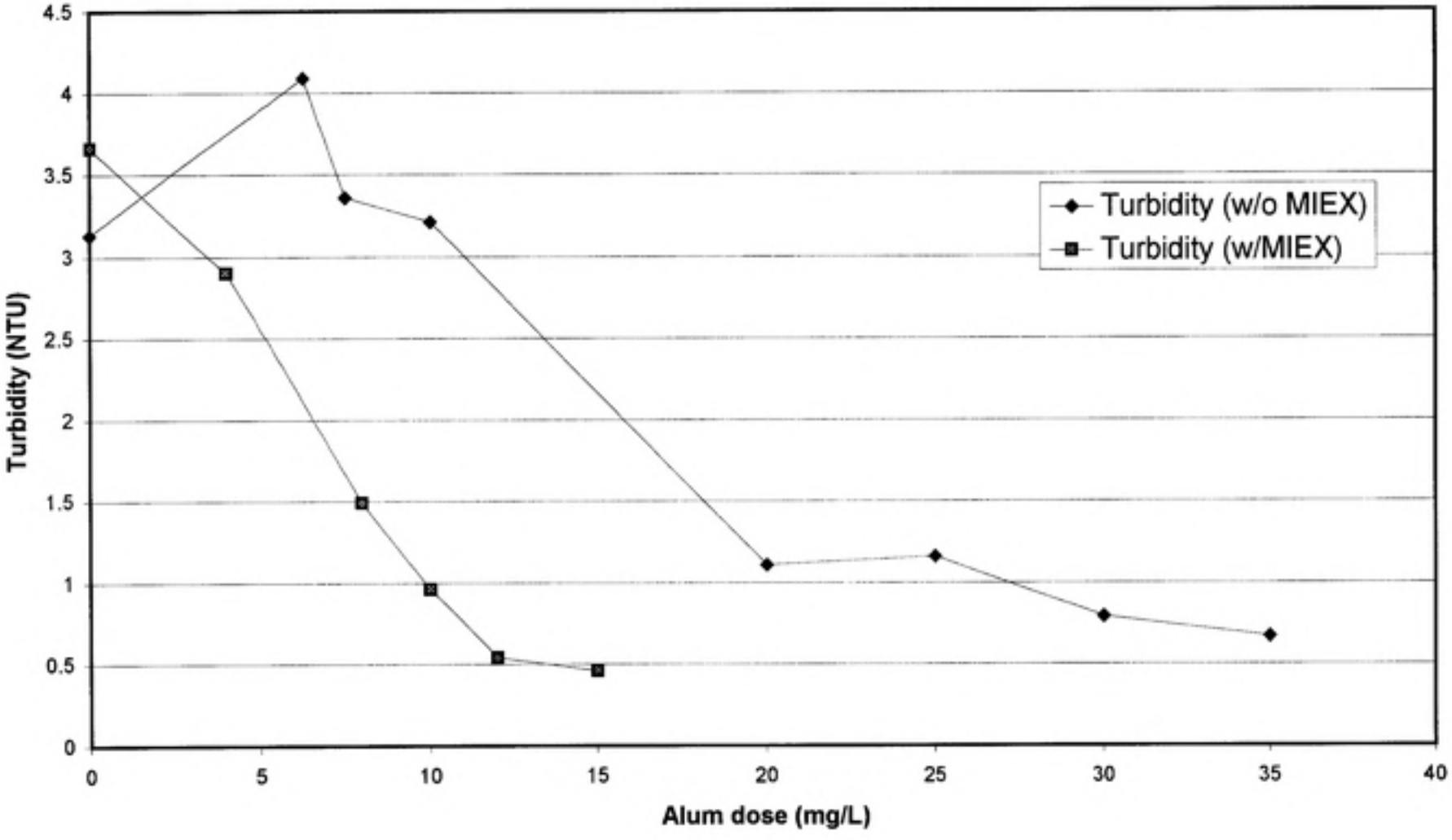

Figure C.4. Turbidity as a Function of Alum Dose for MWD, CA with and without MIEX Pretreatment

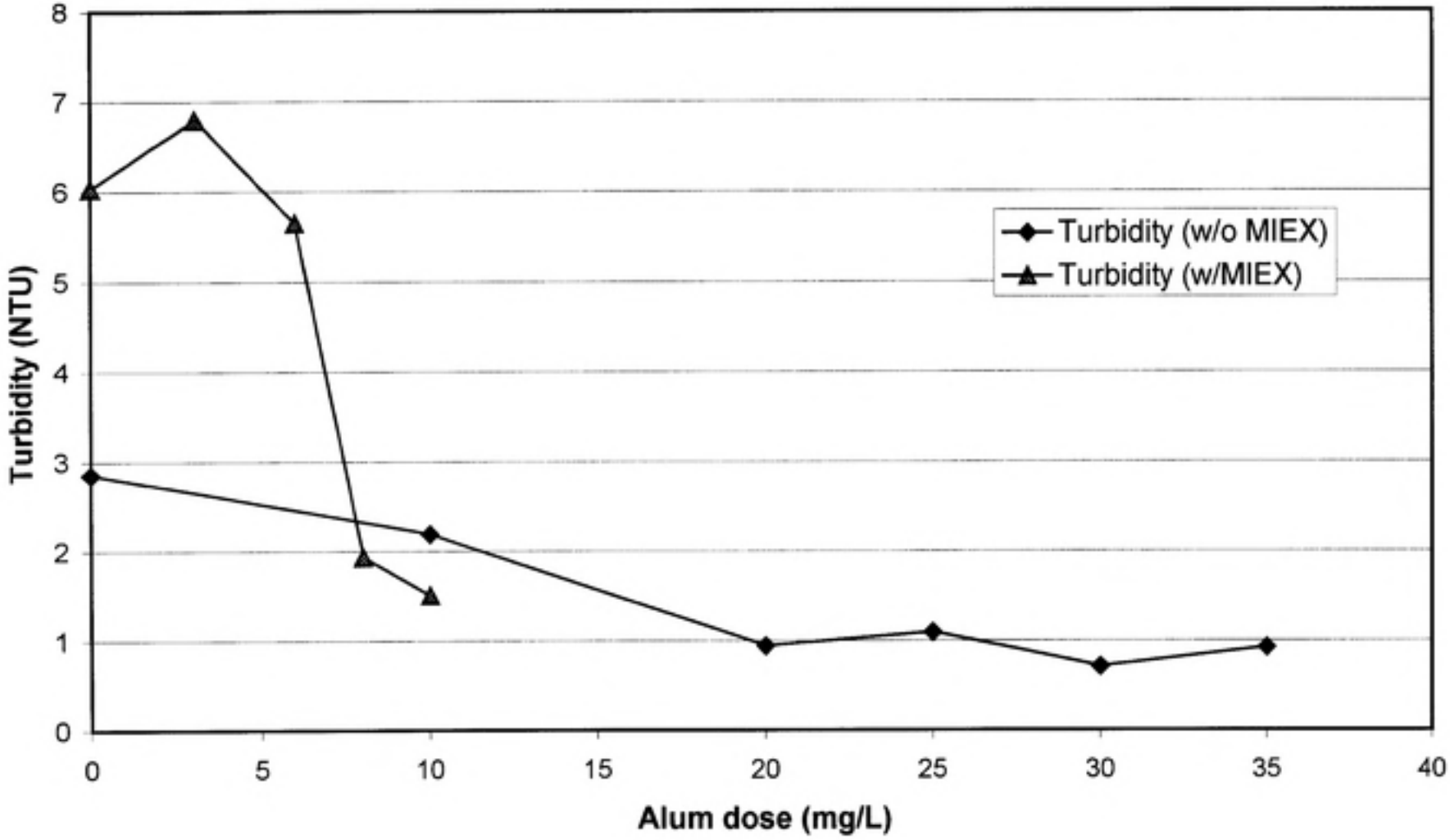

Figure C.5. Turbidity as a function of Alum Dose for Austin, TX with and without MIEX Pretreatment

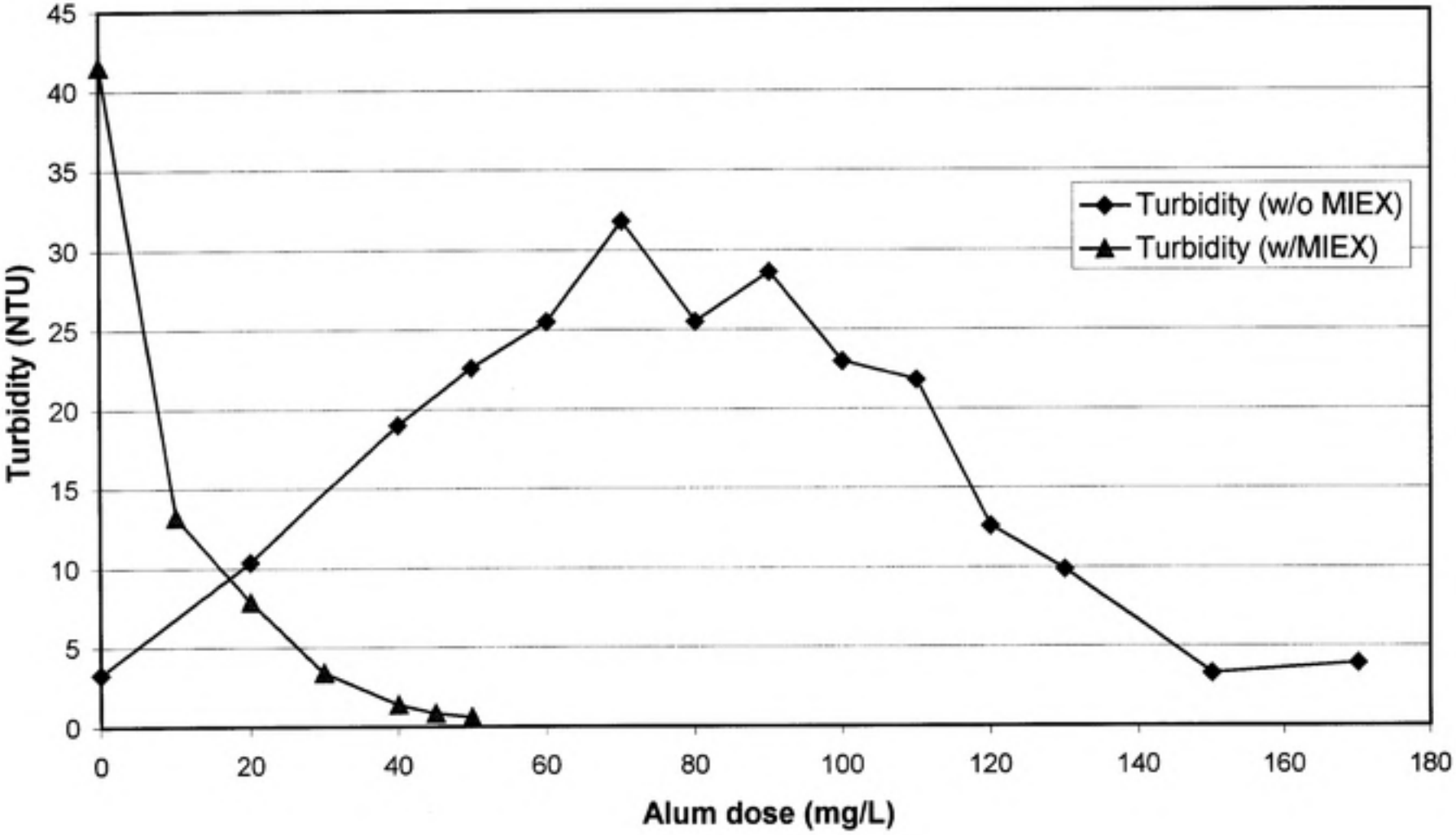

Figure C.6. Turbidity as a Function of Alum dose for Tampa, FL with and without MIEX Pretreatment

APPENDIX D

Table D.1. Assumptions Used in Cost Analysis

Cost Parameter	Explanation	Source
Operating Costs for MIEX		
high estimate	A range of estimates for operating costs were given ($0.14/1000 gal - $0.20/1000 gal). The highest and lowest values of this range were used to create a final range of total costs associated with MIEX. These estimates are likely to encompass the true cost of a MIEX system. Note that the breakdown for this cost is 80% resin, 10% power, and 10% regenerant solution.	Michael Bourke (MB) of Orica
low estimate	$0.14/1000 gal	MB
cost of MIEX based on this estimate (high)	80% of the high estimate (included to show the cost of the MIEX resin alone)	MB
cost of MIEX based on this estimate (low)	80% of the low estimate	MB
disposal of waste regenerant (high)	Assumes off-site disposal as an industrial waste, at a cost of $20-$60/MG of water treated. $40/MG was assumed in this case.	MB
disposal of waste regenerant (low)	Assumes disposal to sanitary sewers at no cost.	MB
Capital Costs for MIEX		
Cost of regeneration system (1979 dollars)	The construction cost for a fixed bed B21ion exchange softening unit was used here for lack of other available information.	EPA's Estimating Water Treatment Costs, Vol. 2, Cost Curves Applicable to 1 to 200 mgd Treatment Plants, 1979

Cost Parameter	Explanation	Source
GDP index for 1979 (1992 is base year = 100)	The gross domestic product (GDP) index compares the value of money each year with respect to the value of a dollar in 1992. This cost index can be used to determine what something would cost to build today based on how much it cost to build the same item in 1979.	Statistical Abstract of the United States
GDP index for 1998	Same as above. There was no data available for the year 2000, so 1998 data was used.	Statistical Abstract of the United States
Cost of regeneration system in 1998	Multiply the cost of regeneration system in 1979*GDP index for 1998 and divide by GDP index for 1979 to get the cost in 1998.	EPA's Estimating Water Treatment Costs, 1979
Cost of mixing tank	Vertical turbine variable speed flocculators were assumed.	Bill Dowbiggin (BD) of CDM-Raleigh
Cost of Sedimentation Tank	Cost is based on a 4-hour detention time and tank with B24sludge scrapers.	BD
Operating Costs for Alum		
mg/L alum used	alum dose used in conventional treatment plant and plant equipped with MIEX	
cost of alum ($/lb)	Alum cost in $/lb	BD
cost of alum ($/d)	lb/d of alum required = 8.34*alum dose (mg/L)*size of plant (MGD)*100%/(8.5%--concentration of alum); multiply this by the cost of alum in $/lb to get cost in $/d	Water Treatment Plant Design, AWWA, 1998
Mass of sludge produced (lb/d)	S = 8.34*Q*(0+B32.44*alum dose + SS concentration); Assume 3 mg/L is SS concentration (based on 1 NTU = 1 mg/L of SS)[a]; Three NTU was assumed to be the turbidity of each source water	[a]Cornwell, 1999
Volume of sludge produced (m^3/yr)	V = (mass solids) / (density water*specific gravity of sludge, 2.32[a] * 3% solids[b]) * 365d/yr	[a]Vandermeyden, 1997 [b]Cornwell, 1999
Volume of sludge (MG/yr)	Multiply previous answer by 0.000264 MG/m^3	

Cost Parameter	Explanation	Source
cost of disposal to sanitary sewers ($/yr)	A linear regression (R^2 = 1) was conducted for cost of disposal ($/yr) and sludge volume (MG/yr). This equation was used to find costs for the specific sludge volumes in the model and then the cost index was used to bring them up to date. 10,000 mg/L was the assumed sludge concentration of SS.	EPA's Estimating Water Treatment Costs, 1979
TOTAL COSTS		
TOTAL CAPITAL	The cost of the regeneration system, the mixing tank, and the sedimentation tank.	
TOTAL OPERATING COSTS (HIGH)	The sum of the high estimate for operating costs for MIEX, the high estimate for the disposal of waste regenerant, the cost of alum and the cost of disposal of alum sludge to sanitary sewers.	
TOTAL OPERATING COSTS (LOW)	The sum of the low estimate for operating costs for MIEX, the low estimate for the disposal of waste regenerant, the cost of alum and the cost of disposal of alum sludge to sanitary sewers.	
Present equivalent cost for the system	The interest rate and number of years in the life cycle are specified. These values are used to calculate the present value equivalent factor (P/A,i,n). This number multiplied by the annual operating costs yields the present value of making "n" number of equal payments (annual operating costs). This number is added to the total capital cost (in the case of the MIEX system) and the total cost is the present equivalent cost for the system.	Pap, Fundamentals of Professional Engineering, 1999

APPENDIX E

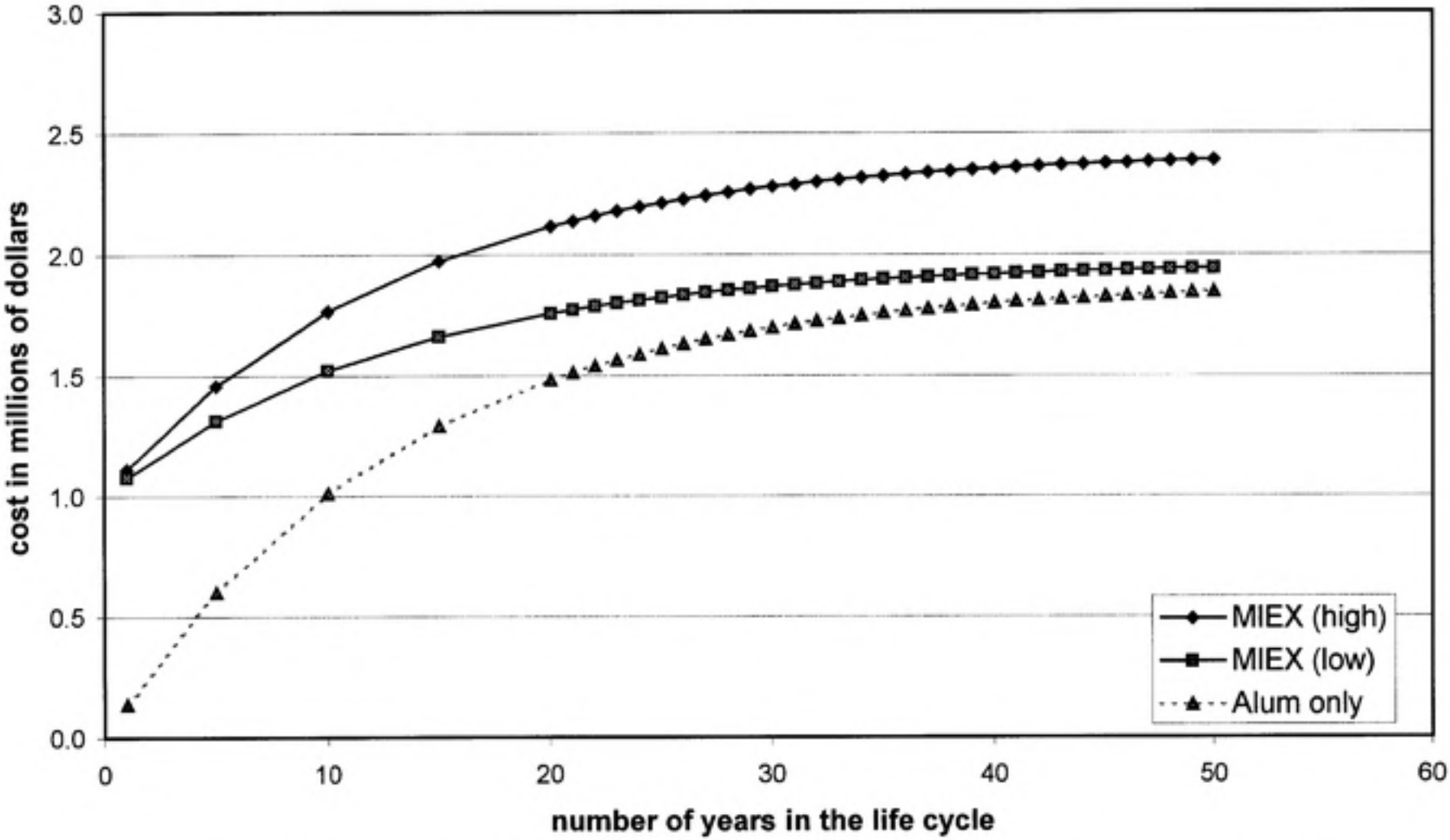

Figure E.1. Present Value of the Life Cycle Costs for a 1 MGD Plant as a function of the number of years in the life cycle (interet rate =8%)

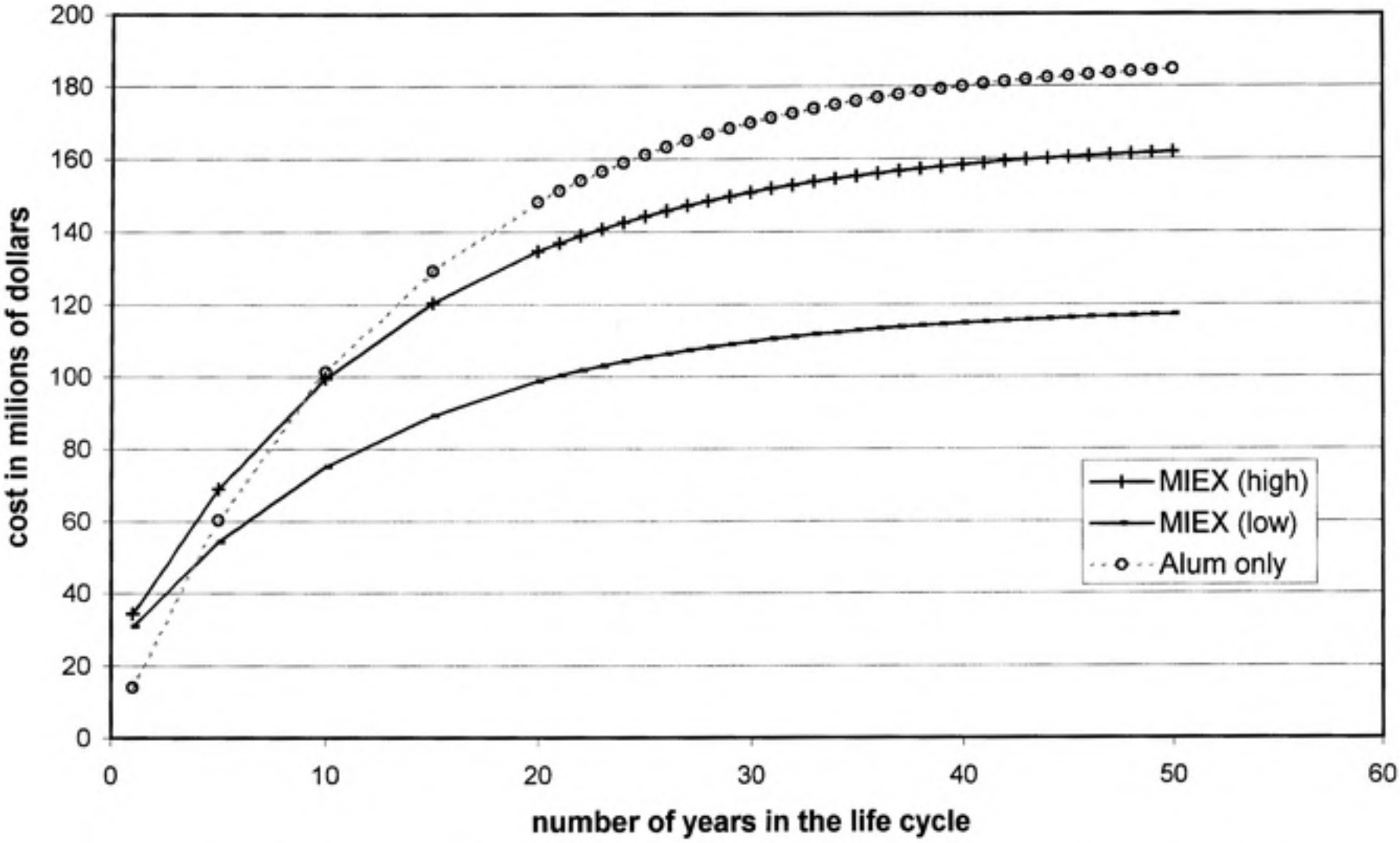

Figure E.2. Present Value of the Life Cycle Costs for a 100 MGD Plant as a function of the number of years in the life cycle (interest rate = 8%)

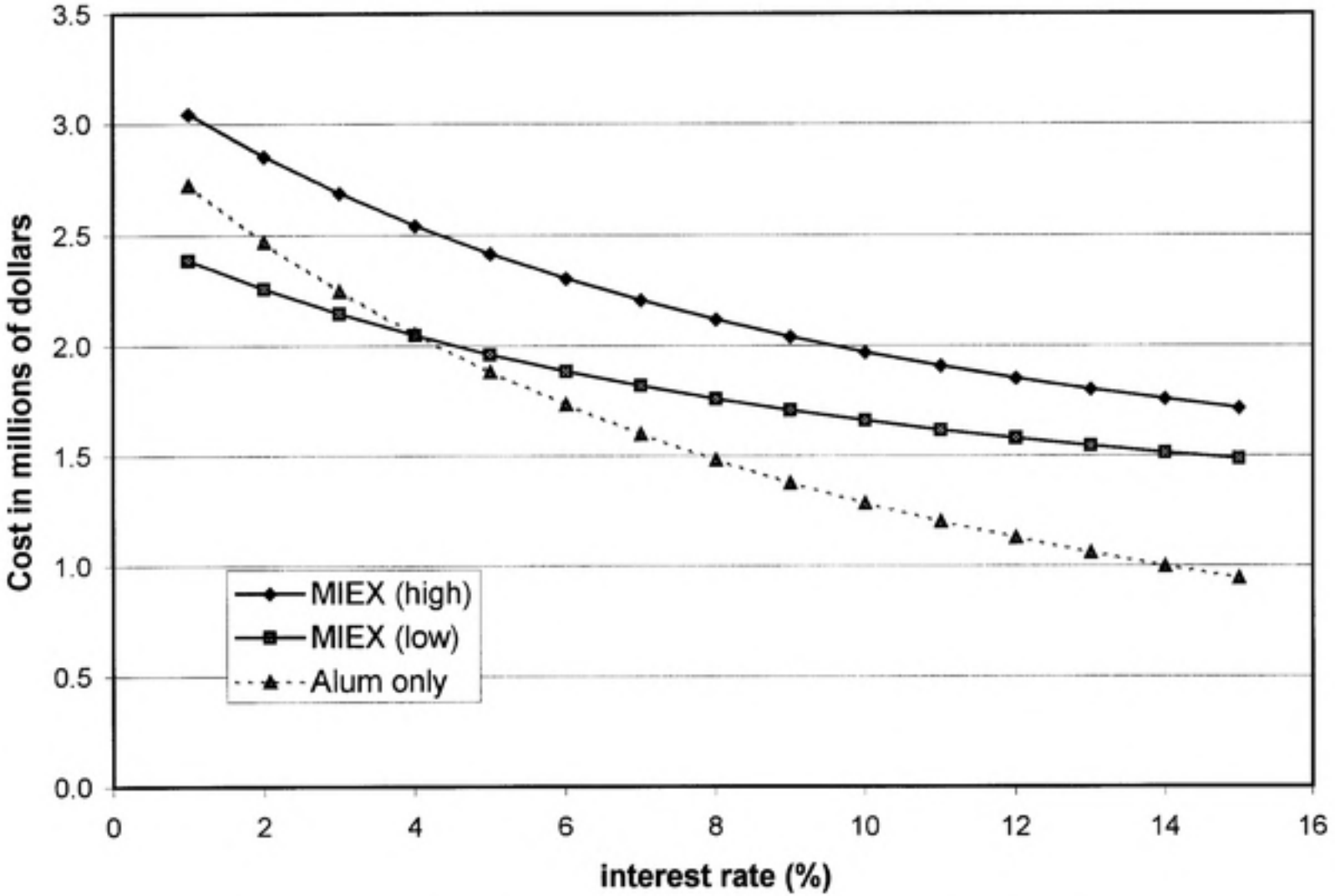

Figure E.3. Present Value of the Life Cycle Cost for a 1 MGD Plant as a function of the interest rate (n=20 years)

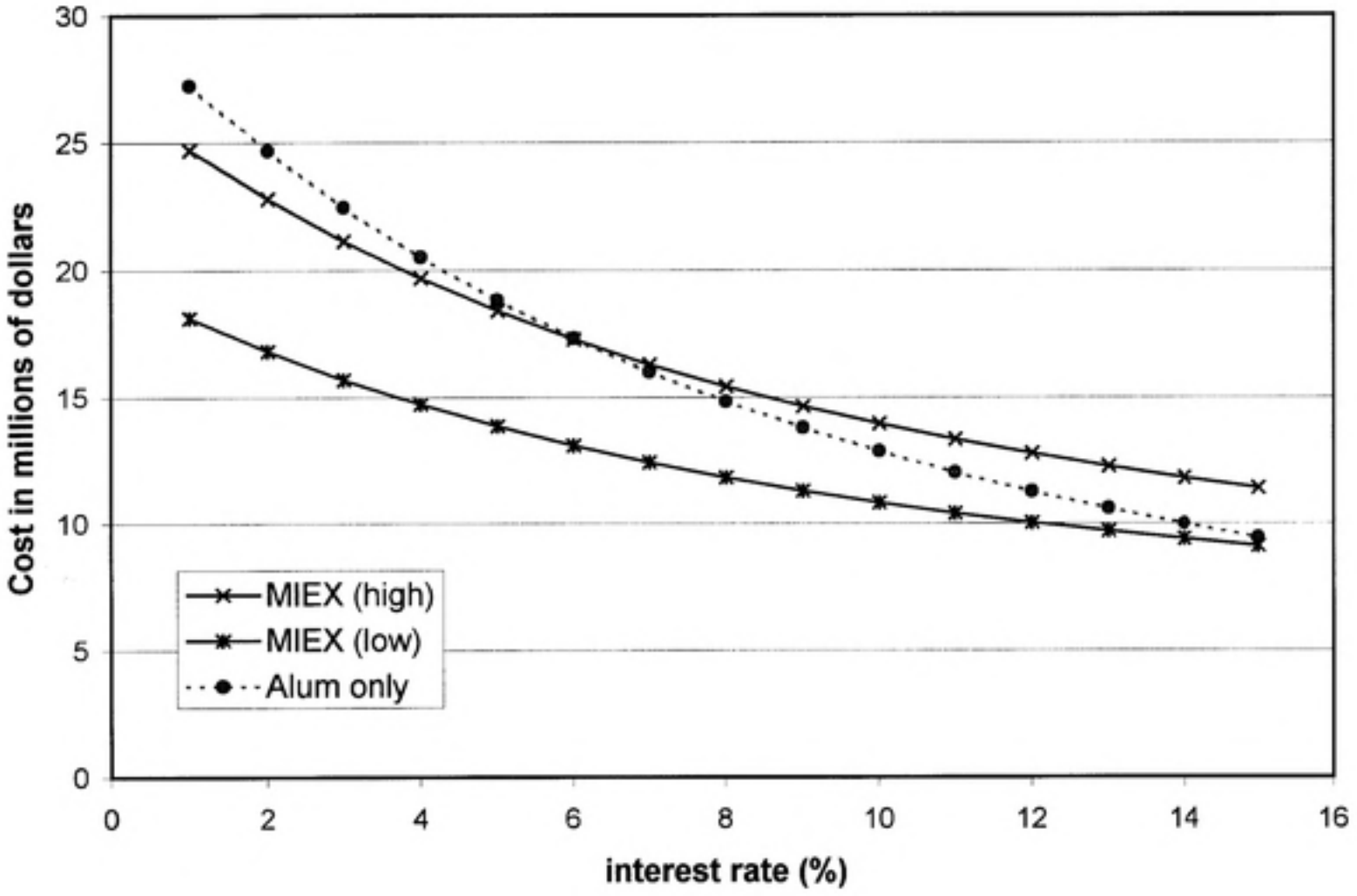

Figure E.4. Present Value of the Life Cycle Costs for a 10 MGD Plant as a function of the interest rate (n = 20 years)

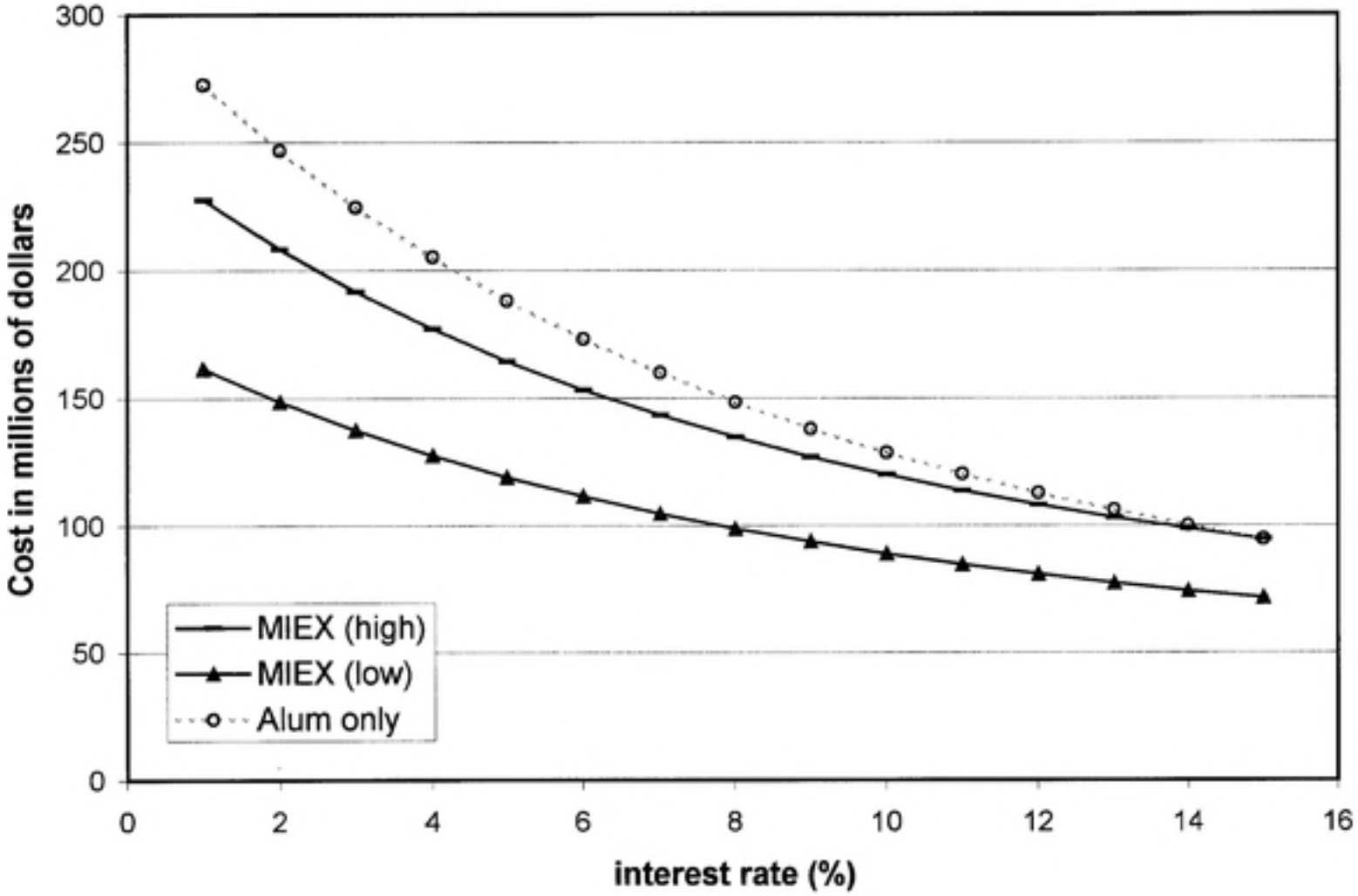

Figure E.5. Present Value of the Life Cycle Costs for a 100 MGD Plant as a function of the interest rate (n = 20 years)